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Class XI and XII

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Regd. Office

406, Taj Apartment, Near Safdarjung Hospital,
Ring Road, New Delhi - 110029.

Managing Editor : Mahabir Singh
Editor : Anil Ahlawat (BE, MBA)

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METHODS OF ANALYSIS

Every research institution and university departments have the Chemistry Division or Department. While, the standard wet analysis is always at hand, the other methods are chromatography, spectrometry—optical, U.V, infrared, X-ray diffraction and X-ray spectrometry. Optical and ultraviolet spectrometers are also combined in some apparatus.

If the spectrometers are mainly handled by physicists, the methods of interpretation will be based on physics. But, most of the apparatus that are used in chemistry departments will be found in physics laboratories also. Advanced theories will be used in physics laboratories but crystallography methods are the same. However, each method itself is treated as if it is completely independent. If precipitates are obtained by the analysis of wet methods, the precipitates should be separated and methods of optical and X-ray spectrometers should be used to not only confirm the analysis but also to do a quantitative test.

Elements obtained in X-ray analysis are not found in the wet analysis method, if the quantity of the element searched for is small; turbidity is taken as the absence of the element searched for. Paper chromatography is a very fast method but not quantitative. Here, cutting the different portions and using X-ray spectrometry for analysis, they can be quantitative also. Spectrometry has an advantage. Each element has its own characteristic lines. Recently, since 1970's, mathematical analysis of X-ray spectrum is quite advanced.

The same method has been used in other regions but this is not generally used because of the rigorous experimentation and analysis of results. Synthesis and analysis are the foundation pillars of chemistry. They can be reinforced by other methods also.

Anil Ahlawat
Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

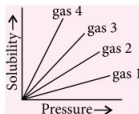
PROBLEM Set 13

JEE MAIN/PMTs

1. A white inorganic solid 'P' on heating with dilute HCl gives a solution 'Q' and gas 'R' with smell of rotten eggs. 'Q' when treated with dilute NaOH gives a white ppt. that dissolves in excess of NaOH. Solution 'Q' is soluble in excess of NH_3 . On strong heating in air 'P' gives a pungent gas 'S' and residue 'T' that dissolves in water. A dilute solution of 'T' gives a white ppt. 'U' on treatment with BaCl_2 solution. The compounds P, Q, R, S, T, and U respectively are

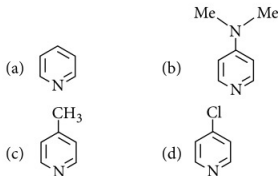
- (a) ZnS , ZnCl_2 , H_2S , SO_2 , ZnSO_4 and BaSO_4
 (b) ZnCl_2 , H_2S , ZnS , SO_2 , ZnSO_4 and BaSO_4
 (c) ZnS , H_2S , ZnCl_2 , SO_2 , ZnSO_4 and BaSO_4
 (d) ZnSO_4 , ZnS , ZnCl_2 , H_2S , SO_2 and BaSO_4

2. The variation of solubility of four different gases in a given solvent with pressure at a constant temperature is shown in the graph. The gas with the highest value of Henry's law constant is



- (a) gas 3 (b) gas 1
 (c) gas 4 (d) gas 2

3. For the reaction, $A \rightleftharpoons nB$ the concentration of A decreases from 0.06 to 0.03 mol L^{-1} and that of B increases from 0 to 0.06 mol L^{-1} at equilibrium. The value of n and the equilibrium constant for the reaction, respectively are
 (a) 2 and 0.12 (b) 2 and 1.2
 (c) 3 and 0.12 (d) 3 and 1.2
4. Among the following substituted pyridines, the most basic compound is



5. The radii of the first Bohr orbit of $\text{H}(r_{\text{H}})$, $\text{He}^+(r_{\text{He}^+})$ and $\text{Li}^{2+}(r_{\text{Li}^{2+}})$ are in the order
 (a) $r_{\text{He}^+} > r_{\text{H}} > r_{\text{Li}^{2+}}$ (b) $r_{\text{H}} < r_{\text{He}^+} < r_{\text{Li}^{2+}}$
 (c) $r_{\text{H}} > r_{\text{He}^+} > r_{\text{Li}^{2+}}$ (d) $r_{\text{He}^+} < r_{\text{H}} < r_{\text{Li}^{2+}}$

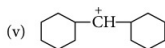
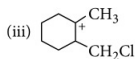
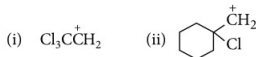
Solution Senders of Chemistry Musing

SET 12

1. Khwaja Sami Baig, Azamgarh (UP)
 2. Devjit Acharyee, Kolkata (West Bengal)

JEE ADVANCED

6. The increasing order of the stability of given carbocations will be



- (a) $i < ii < iv < v < iii$
 (b) $i < ii < v < iv < iii$
 (c) $ii < i < v < iv < iii$
 (d) $ii < v < i < iii < iv$

COMPREHENSION

Xenon, because of its lowest ionisation energy in its group, can form compounds with oxygen and fluorine. The compounds XeF_2 , XeF_4 and XeF_6 are all white solids. They can be sublimed at room temperature, and can be stored indefinitely in nickel containers. The lower fluorides form higher fluorides when heated with F_2 under pressure. The fluorides are all

extremely strong oxidising and fluorinating agents.

The fluorides differ in their reactivity with water. XeF_2 is soluble in water, but undergoes slow hydrolysis. XeF_4 and XeF_6 react violently with water.

7. Xenon hexafluoride reacts with potassium fluoride to yield
 (a) $[\text{XeF}_5]^+[\text{KF}_2]^-$ (b) $\text{K}^+[\text{XeF}_7]^-$
 (c) XeF_4 (d) none of these.
8. A fluoride of xenon (A) on hydrolysis gives a compound (B) which has trigonal pyramidal structure. (A) and (B) respectively are
 (a) XeF_2 , XeO_2F_2 (b) XeF_6 , XeO_3
 (c) XeF_4 , XeOF_4 (d) XeF_2 , XeO_4

INTEGER VALUE

9. A solution of 500 mL of 0.2 M KOH and 500 mL of 0.2 M HCl is mixed and stirred, the rise in temperature is t_1 . The experiment is repeated using 250 mL of each of the solution; the temperature rise is t_2 . The ratio t_1/t_2 is
10. The half-lives of two samples of the same substance are 50 and 200 s at 0.4 M and 0.1 M concentrations, respectively. The order of reaction is

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EXAMINER'S MIND NCERT^{CLASS} XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

STATES OF MATTER | THERMODYNAMICS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- The solubility of a gas in water at 300 K under a pressure of 100 atmospheres is $4 \times 10^{-3} \text{ kg L}^{-1}$. Therefore, the mass of the gas (in kg) dissolved in 250 mL of water under a pressure of 250 atmospheres at 300 K is
(a) 2.5×10^{-3} (b) 2.0×10^{-3}
(c) 1.25×10^{-3} (d) 5.0×10^{-3}
- The pressure-volume work for an ideal gas can be calculated by using the expression $W = - \int_{V_i}^{V_f} P_{\text{ex}} dV$. The work can also be calculated from the PV -plot by using the area under the curve within the specified limits. When an ideal gas is compressed (i) reversibly or (ii) irreversibly from volume V_i to V_f . Choose the correct option.
(a) $W_{\text{reversible}} = W_{\text{irreversible}}$
(b) $W_{\text{reversible}} < W_{\text{irreversible}}$
(c) $W_{\text{reversible}} > W_{\text{irreversible}}$
(d) $W_{\text{reversible}} = W_{\text{irreversible}} + P_{\text{ex}} \Delta V$
- Pick out the wrong statement(s).
(i) Vapour pressure of a liquid is the measure of the strength of intermolecular attractive forces.
(ii) Surface tension of a liquid acts perpendicular to the surface of the liquid.

- (iii) Vapour pressure of all liquids is same at their freezing points.
(iv) Liquids with stronger intermolecular attractive forces are more viscous than those with weaker intermolecular force.
(a) (ii), (iii) and (iv) (b) (ii) and (iii)
(c) (i), (ii) and (iii) (d) (iii) only
- Under which of the following conditions, the reaction is always feasible?
(a) $\Delta H = T\Delta S$
(b) ΔH (+ve), $T\Delta S$ (-ve)
(c) ΔH (-ve), $T\Delta S$ (+ve)
(d) ΔH (-ve), $T\Delta S$ (-ve)
- What is the effect on the pressure of a gas if its temperature is increased at constant volume?
(a) The pressure of the gas increases.
(b) The pressure of the gas decreases.
(c) The pressure of the gas remains same.
(d) The pressure of the gas becomes double.
- The standard enthalpy of the decomposition of N_2O_4 to NO_2 is 58.04 kJ and standard entropy of this reaction is 176.7 J/K. The standard free energy change for this reaction at 25°C is
(a) -538 kJ (b) 538 kJ
(c) -5.38 kJ (d) 5.38 kJ
- If the rate of diffusion of A is 5 times that of B, what will be the ratio of the densities of A and B?
(a) 25 (b) 1/25
(c) 5 (d) 1/5

8. If enthalpies of formation for $\text{C}_2\text{H}_{4(g)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$ at 25°C and 1 atm pressure are 52, -394 and -286 kJ/mol respectively, then enthalpy of combustion of $\text{C}_2\text{H}_{4(g)}$ will be
 (a) -141.2 kJ/mol (b) +14.2 kJ/mol
 (c) +141.2 kJ/mol (d) -1412 kJ/mol

9. At what pressure will a quantity of gas, which occupies 100 mL at a pressure of 720 mm, occupy a volume of 85 mL?
 (a) 736.18 mm (b) 820.20 mm
 (c) 784.15 mm (d) 847.06 mm

10. What will be the change in internal energy when 12 kJ of work is done on the system and 2 kJ of heat is given by the system?
 (a) +10 kJ (b) -10 kJ
 (c) +5 kJ (d) -5 kJ

11. The units of van der Waals constants a and b respectively are
 (a) $\text{L atm}^2 \text{mol}^{-1}$ and mol L^{-1}
 (b) L atm mol^2 and mol L
 (c) $\text{L}^2 \text{atm mol}^{-2}$ and $\text{mol}^{-1} \text{L}$
 (d) $\text{L}^{-2} \text{atm}^{-1} \text{mol}^{-1}$ and L mol^{-2}

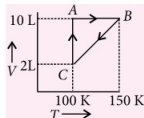
12. The enthalpy of formation of ammonia when calculated from the following bond energy data is (B.E. of N-H, H-H, $\text{N}\equiv\text{N}$ is 389 kJ mol^{-1} , 435 kJ mol^{-1} , 945.36 kJ mol^{-1} respectively)
 (a) -41.82 kJ mol^{-1} (b) +83.64 kJ mol^{-1}
 (c) -945.36 kJ mol^{-1} (d) -833 kJ mol^{-1}

13. Under what conditions gases generally deviate from ideal behaviour?
 (a) At high temperature and low pressure
 (b) At low temperature and high pressure
 (c) At high temperature and high pressure
 (d) At low temperature and low pressure

14. For a reaction, $2\text{K}_{(g)} + \text{L}_{(g)} \rightarrow 2\text{M}_{(g)}$; $\Delta U^\circ = -10.5 \text{ kJ}$ and $\Delta S^\circ = -44.1 \text{ J K}^{-1}$. Calculate ΔG° for the reaction and predict whether the reaction will be spontaneous or non-spontaneous?
 (a) +0.16 kJ, non-spontaneous
 (b) -0.16 kJ, spontaneous
 (c) +26.12 kJ, non-spontaneous
 (d) -26.12 kJ, spontaneous

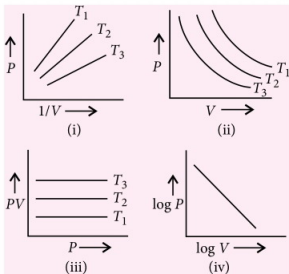
15. Volume occupied by 7 g of nitrogen gas at 27°C and 750 mm Hg pressure is
 (a) 6.14 litres (b) 8.24 litres
 (c) 5.24 litres (d) 6.24 litres

16. Consider the given diagram for 1 mole of a gas:



The process $A \rightarrow B$ represents

- (a) isobaric change (b) isothermal change
 (c) adiabatic change (d) isochoric change.
17. Graphs between pressure and volume are plotted at different temperatures. Which of the following isotherms represents Boyle's law, $PV = \text{constant}$?



- (a) Only (ii) (b) Only (iv)
 (c) All of these. (d) None of these.
18. Which of the following statements is correct?
 (a) The presence of reacting species in a covered beaker is an example of open system.
 (b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
 (c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
 (d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

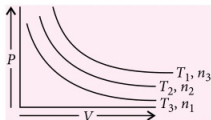
19. 50 mL of hydrogen diffuses out through a small hole of a vessel, in 20 minutes. The time taken by 40 mL of oxygen to diffuse out is
- (a) 32 minutes (b) 64 minutes
(c) 8 minutes (d) 12 minutes
20. Identify the correct statement regarding entropy.
- (a) At absolute zero temperature, the entropy of all crystalline substances is taken to be zero.
(b) At absolute zero temperature, the entropy of a perfectly crystalline substance is positive.
(c) At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero.
(d) At 0°C , the entropy of a perfectly crystalline substance is taken to be zero.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. For the reaction between CO_2 and graphite,
 $\text{CO}_{2(g)} + \text{C}_{(s)} \rightarrow 2\text{CO}_{(g)}$;
 $\Delta H = 170 \text{ kJ}$ and $\Delta S = 170 \text{ J K}^{-1}$. The reaction will be non-spontaneous at
- (a) 300 K (b) 500 K
(c) 900 K (d) 1100 K
22. The graph of P vs V is given at different temperatures and number of moles :

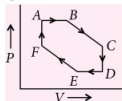


The correct relationship is/are

- (a) $T_1 > T_2 > T_3$ (b) $T_1 < T_2 < T_3$
(c) $n_1 > n_2 > n_3$ (d) $n_3 > n_2 > n_1$
23. Which of the following statements are correct?
- (a) Z (compressibility factor) for ideal gas is independent of temperature and pressure.
(b) Z for ideal gas is greater than one.

- (c) Z for non-ideal gas is either greater than one or less than one as well as dependent on temperature and pressure.
(d) when $Z > 1$, then force of attraction dominates over force of repulsion.

24. Which inferences have been accurately drawn from the given plot?



(Temperature at A, B and F is T_1 and at C, D and E is T_2 . $T_1 > T_2$)

- (a) $B \rightarrow C$ is an adiabatic expansion and temperature falls from T_1 to T_2 .
(b) $E \rightarrow F$ is an adiabatic compression and temperature increases from T_2 to T_1 .
(c) $F \rightarrow A$ is an isothermal and isochoric process.
(d) $C \rightarrow D$ is an adiabatic and isobaric process.
25. For the non-zero value of force of attraction between gas molecules and zero volume of gas molecules, gas equation will be

- (a) $PV = nRT - \frac{n^2a}{V}$ (b) $PV = nRT + nbP$
(c) $PV = nRT$ (d) $P = \frac{nRT}{V-b}$

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Thermodynamic function, the Gibbs energy or Gibbs function, G , is defined as

$$G = H - TS$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

Usually the subscript 'system' is dropped and we simply write this equation as

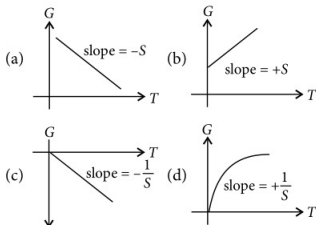
$$\Delta G = \Delta H - T\Delta S$$

Here, we have considered both terms together for spontaneity, energy (in terms of ΔH) and entropy (ΔS , a measure of disorder).

26. When enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^3 \text{ cal mol}^{-1}$ and $7.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively predict the reaction at 298 K is

- (a) irreversible (b) reversible
(c) spontaneous (d) non-spontaneous.

27. For a pure substance, a plot of Gibbs free energy (G) against temperature at constant pressure is



28. For a spontaneous reaction the ΔG , equilibrium constant (K) and E_{cell}° will be respectively
(a) $-ve$, >1 , $+ve$ (b) $+ve$, >1 , $-ve$
(c) $-ve$, <1 , $-ve$ (d) $-ve$, >1 , $-ve$

Paragraph for Questions 29 to 31

Real gases do not follow ideal gas equation perfectly under all conditions.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z , which is the ratio of product PV and nRT . Mathematically,

$$Z = \frac{PV}{nRT}$$

29. Dominance of strong repulsive forces among the molecules of the gas
(a) depends on Z and indicated by $Z = 1$
(b) depends on Z and indicated by $Z > 1$
(c) depends on Z and indicated by $Z < 1$
(d) is independent of Z .

30. For a real gas, the compressibility factor Z has different values at different temperatures and pressures. Which of the following is not correct under the given conditions?

- (a) $Z = 1$ at very low pressure.
(b) $Z > 1$ at high pressure.
(c) $Z = 1$ under all conditions.
(d) $Z < 1$ at intermediate pressure.

31. It is observed that H_2 and He gases always show positive deviation from ideal behaviour i.e., $Z > 1$. This is because

- (a) the value of a is very large due to high attractive forces
(b) the weak intermolecular forces of attraction due to which a is very small and a/V^2 is negligible
(c) the value of b is very large due to large size of the molecules
(d) both a and b are very small and negligible.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	1. $\Delta_{\text{sol}}H^{\circ}$
Q. $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	2. $\Delta_{\text{lattice}}H^{\circ}$
R. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	3. $\Delta_{\text{f}}H^{\circ}$
S. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	4. $\Delta_{\text{a}}H^{\circ}$

P	Q	R	S
(a) 4	3	1	2
(b) 2	1	4	3
(c) 1	2	3	4
(d) 3	4	2	1

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I (Molecules)		List II (Intermolecular forces)	
P.	H ₂ S molecules	1.	London dispersion forces
Q.	Cl ₂ and CCl ₄ molecules	2.	Dipole-induced dipole forces
R.	Ethyl amine molecules	3.	Dipole-dipole interactions
S.	He atoms and HCl molecules	4.	Hydrogen bonding
P	Q	R	S
(a)	1	2	3
(b)	3	1	4
(c)	4	2	1
(d)	4	3	2

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I		List II	
P.	2N ₂ O _(g) → 2N _{2(g)} + O _{2(g)} + Heat	1.	Spontaneous at low temperature
Q.	H ₂ O _(g) → H ₂ O _(l)	2.	Spontaneous at high temperature
R.	2NH _{3(g)} + Heat → N _{2(g)} + 3H _{2(g)}	3.	Non-spontaneous at all temperatures
S.	3O _{2(g)} + Heat → 2O _{3(g)}	4.	Spontaneous at all temperatures
P	Q	R	S
(a)	3	1	2
(b)	4	1	3
(c)	3	4	2
(d)	4	1	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- If both assertion and reason are true and reason is the correct explanation of assertion.
 - If both assertion and reason are true but reason is not the correct explanation of assertion.
 - If assertion is true but reason is false.
 - If both assertion and reason are false.
35. **Assertion** : Compressibility factor (Z) is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.
Reason : At high pressure all the gases have $Z < 1$ and can be easily compressed.
36. **Assertion** : Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
Reason : Entropy of the system increases with increase in temperature.
37. **Assertion** : The value of van der Waals constant ' a ' is larger for NH₃ than PH₃.
Reason : Hydrogen bonding is present in NH₃.
38. **Assertion** : The solubility of most salts in water increases with rise of temperature.
Reason : For most of the ionic compounds, $\Delta_{\text{sol}}H^\circ$ is positive and the dissolution process is endothermic.
39. **Assertion** : Greater the value of van der Waals constant ' a ', easier is the liquifaction of a gas.
Reason : ' a ' indirectly measures the magnitude of attractive forces between the molecules.
40. **Assertion** : Work done during free expansion of an ideal gas whether reversible or irreversible is positive.
Reason : During free expansion, external pressure is always less than the pressure of the system.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

- 2 g of a gas A is introduced into an evacuated flask kept at 25°C. The pressure is found to be 1 atm. If 3 g of another gas B is added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal behaviour, the ratio of molecular weights of M_B and M_A is
- Change in internal energy when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system, is

43. A 4 : 1 molar mixture of He and CH₄ is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The composition of the mixture effusing out initially is in the ratio $x : y$. The value of $(x + y)$ is

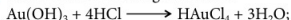
44. For the reaction $A_{(s)} + 3B_{(g)} \longrightarrow 4C_{(s)} + D_{(l)}$, ΔH and ΔU are related as $\Delta H = \Delta U - xRT$. The value of x is

45. 92.0 g of N₂O_{4(g)} at 27°C is placed in a closed vessel under one atmosphere. When heated to 327°C, N₂O_{4(g)} dissociates into NO_{2(g)} to the extent of 50% by mass. The resultant pressure (atm) of the gaseous system is

46. Given that, $S^\circ_{H_2} = 131 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ_{Cl_2} = 223 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S^\circ_{HCl} = 183 \text{ J K}^{-1} \text{ mol}^{-1}$. The standard entropy change in the formation of 1 mole of HCl_(g) from H_{2(g)} and Cl_{2(g)} will be

47. The ratio of rate of diffusion of helium and methane under identical conditions of pressure and temperature is

48. Consider the following reactions :



$$\Delta H = -28 \text{ kcal}$$

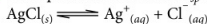


$$\Delta H = -36.8 \text{ kcal}$$

If 1 mole of HAuBr₄ was mixed with 4 moles of HCl, 0.44 kcal heat was absorbed. The fraction of HAuBr₄ converted into HAuCl₄ is $x \times 10^{-2}$. The value of x is

49. The root mean square speed of ethane at 27°C and 720 mm of Hg is $x \times 10^4$ cm/sec. The value of x is

50. The equilibrium constant K_{sp} for the reaction



is found to be $x \times 10^{-10}$ using the data $\Delta G^\circ_f(\text{AgCl}) = -109.4 \text{ kJ}$, $\Delta G^\circ_f(\text{Ag}^+) = 77.1 \text{ kJ}$ and $\Delta G^\circ_f(\text{Cl}^-) = -131.2 \text{ kJ}$. The value of x is

SOLUTIONS

1. (a) : Let $P_1 = 100 \text{ atm}$, $T_1 = 300 \text{ K}$
Since solubility is given as $4 \times 10^{-3} \text{ kg L}^{-1}$, it means that $4 \times 10^{-3} \text{ kg}$ of the gas has been dissolved in 1000 mL of water.

$$\therefore V_1 = 1000 \text{ mL}, w_1 = 4 \times 10^{-3} \text{ kg}$$

Also given, $P_2 = 250 \text{ atm}$, $V_2 = 250 \text{ mL}$, $T_2 = 300 \text{ K}$, $w_2 = ?$

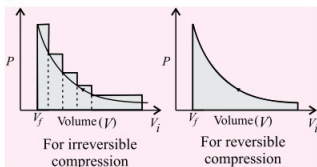
From ideal gas equation, $\frac{P_1 V_1}{n_1} = \frac{P_2 V_2}{n_2}$

$$\text{or } \frac{P_1 V_1}{w_1} = \frac{P_2 V_2}{w_2}$$

$$\therefore \frac{100 \times 1000}{4 \times 10^{-3}} = \frac{250 \times 250}{w_2}$$

$$w_2 = \frac{250 \times 250 \times 4 \times 10^{-3}}{100 \times 1000} = 2.5 \times 10^{-3} \text{ kg}$$

2. (b) :



In both the curves, work done on the gas is represented by the shaded area and the area under the curve is always more in irreversible compression.

Hence, $W_{\text{irreversible}} > W_{\text{reversible}}$

3. (d) : Vapour pressure of all liquids are different at their freezing points.

4. (c) : Feasibility of reaction is determined by free energy change value (ΔG).

ΔG is given by Gibbs equation :

$$\Delta G = \Delta H - T\Delta S$$

Reaction is feasible if ΔG value is negative. Therefore, if ΔH is negative and $T\Delta S$ is positive then the ΔG will always be negative and the reaction will always be feasible.

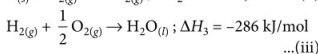
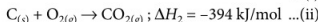
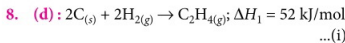
5. (a) : With increase in temperature at constant volume the pressure of the gas increases.

6. (d) : $\Delta H^\circ = 58.04 \text{ kJ} = 58.04 \times 10^3 \text{ J}$
 $\Delta S^\circ = 176.7 \text{ J/K}$, $T = 273 + 25 = 298 \text{ K}$
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 58040 - 298 \times 176.7$
 $= 5383.4 \text{ J} = 5.38 \text{ kJ}$

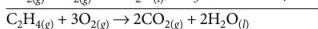
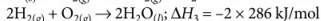
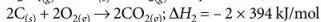
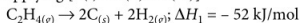
$$7. \text{ (b): Rate of diffusion} \propto \frac{1}{\sqrt{\text{Density}}}$$

$$\Rightarrow \frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \sqrt{\frac{\text{Density of B}}{\text{Density of A}}}$$

$$\Rightarrow 5 = \sqrt{\frac{\text{Density of B}}{\text{Density of A}}} \Rightarrow \frac{\text{Density of A}}{\text{Density of B}} = \frac{1}{25}$$



The combustion of C_2H_4 can be calculated by applying $[-(i) + 2(ii) + 2(iii)]$



$$\Delta H = -\Delta H_1 + 2\Delta H_2 + 2\Delta H_3$$

$$\Rightarrow \Delta H = -52 - 2 \times 394 - 2 \times 286 = -1412 \text{ kJ/mol}$$

9. (d): According to Boyle's law, at constant temperature

$$P_1 V_1 = P_2 V_2 \Rightarrow 720 \times 100 = P_2 \times 85$$

$$P_2 = \frac{72000}{85} = 847.06 \text{ mm}$$

10. (a): Heat evolved = -2 kJ

Work done on the system = +12 kJ

$$\Delta U = q + w = -2 + 12 = +10 \text{ kJ}$$

11. (c): a and b are expressed in terms of the units of P and V .

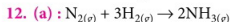
$$\text{Pressure correction} = P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P' V^2}{n^2} = \frac{\text{pressure} \times (\text{volume})^2}{(\text{mol})^2}$$

$$\text{Unit of } a = \text{atm L}^2 \text{ mol}^{-2}$$

Unit of b is the same as for the volume, i.e., L mol^{-1} .

$$V' = nb \Rightarrow b = \frac{V'}{n} = \text{L mol}^{-1}$$



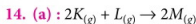
$$\Delta_f H = B.E. (\text{N} \equiv \text{N}) + 3 \times B.E. (\text{H} - \text{H})$$

$$-2 \times 3B.E. (\text{N} - \text{H})$$

$$= 945.36 + 3 \times 435.0 - 6 \times 389.0 = -83.64 \text{ kJ}$$

$$\text{Enthalpy of formation of } \text{NH}_3 = \frac{-83.64}{2} = -41.82 \text{ kJ/mol}$$

13. (b): At low temperature and high pressure, the volume of the particles is not negligible as compared to the total volume of the gas. Also, the intermolecular forces start acting upon the molecules. Hence, they deviate from ideal behaviour.



$$\Delta n_g = 2 - 3 = -1$$

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$= -10.5 \times 10^3 + (-1 \times 8.314 \times 298)$$

$$= -10500 + (-2477.572) = -12977.57 \text{ J}$$

$$= -12.98 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -12.98 - 298 (-44.1 \times 10^{-3})$$

$$= -12.98 + 13.14 = 0.16 \text{ kJ}$$

Since ΔG° is +ve hence, the reaction is non-spontaneous.

15. (d): Weight of nitrogen gas = 7 g;

$$T = 27^\circ\text{C} = 300 \text{ K and}$$

$$P = 750 \text{ mm Hg} = \frac{750}{760} \text{ atm}$$

Molecular mass of nitrogen gas is 28 and number of moles of the gas,

$$n = \frac{\text{Weight of nitrogen}}{\text{Molecular mass}} = \frac{7}{28} = 0.25$$

Therefore, volume occupied by the nitrogen gas,

$$V = \frac{nRT}{P} = \frac{0.25 \times 0.0821 \times 300}{750/760} = 6.24 \text{ litres}$$

16. (d): There is no change in volume from $A \rightarrow B$.

17. (c)

18. (c): In a closed system (e.g., the presence of reactants in a closed vessel made of conducting material i.e. copper) there is no exchange of matter, but exchange of energy is possible between system and the surroundings.

19. (b): Volume of hydrogen = 50 mL;

Time taken for diffusion of hydrogen = 20 min

Volume of oxygen = 40 mL

$$\text{Rate of diffusion of hydrogen } (r_1) = \frac{50}{20}$$

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= 2.5 mL/min and rate of diffusion of oxygen

$$(r_2) = \frac{40}{t} \text{ mL/min}$$

Since the molecular mass of hydrogen (M_1) = 2 and that of oxygen (M_2) = 32, therefore,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{2.5}{40/t} = \sqrt{\frac{32}{2}}$$
$$\Rightarrow \frac{t}{16} = 4 \Rightarrow t = 64 \text{ minutes}$$

20. (c) : This is the statement of third law of thermodynamics. In a perfect crystal, at absolute zero temperature, each constituent of lattice must have the lowest energy, so it leads to perfect order, therefore, zero entropy.

21. (a, b, c) : For equilibrium $\Delta G = 0 = \Delta H - T\Delta S$,

$$T = \frac{\Delta H}{\Delta S} = \frac{170 \times 10^3}{170} = 1000 \text{ K}$$

The reaction would be non-spontaneous at temperature less than 1000 K, so as to have ΔG positive.

22. (a, d) : If temperature is high, then pressure and volume would be high. If number of moles are large, then again pressure and volume would be high. Hence, $T_1 > T_2 > T_3$ and $n_3 > n_2 > n_1$.

23. (a, c) : For ideal gas, compressibility factor, $Z = 1$ at all temperatures and pressures. When $Z > 1$, then force of repulsion dominates over force of attraction.

24. (a, b, c) : $C \rightarrow D$ is an isochoric and isothermal.

25. (a) : For n moles of a real gas,

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

when $\frac{n^2 a}{V^2} \neq 0$ and $b = 0$

$$\left(P + \frac{n^2 a}{V^2} \right) V = nRT$$

$$PV + \frac{n^2 a}{V} = nRT \quad PV = nRT - \frac{n^2 a}{V}$$

26. (c) : Enthalpy change, $\Delta H = -2.5 \times 10^3 \text{ cal mol}^{-1}$
Entropy change, $\Delta S = 7.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$
 $T = 298 \text{ K}$

As, $\Delta G = \Delta H - T\Delta S$

$$\Delta G = -2.5 \times 10^3 - 298 \times 7.4$$
$$= -4.70 \times 10^3 \text{ cal mol}^{-1}$$

For spontaneity of reaction, negative value of ΔG is required, so the reaction is spontaneous.

27. (a) : $G = H - TS$

$$y = c + mx \quad \therefore m = -S$$

28. (a) : For spontaneous process,

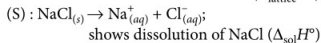
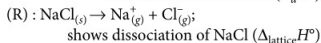
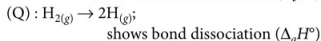
$$\Delta G = -ve, K > 1 \text{ and } E_{\text{cell}}^{\circ} = +ve.$$

29. (b) : When the value of $Z < 1$, it is due to attractive forces between the molecules. At high pressure, when $Z > 1$, it is due to repulsive forces between electron clouds of the molecules of gases.

30. (c) : $Z = 1$ under all conditions for an ideal gas not for real gas.

31. (b) : Due to weak intermolecular forces of attraction, H_2 and He gases show the value of $Z > 1$.

32. (d) : (P) : $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$;
shows combustion reaction ($\Delta_c H^{\circ}$)



33. (b)

34. (d) : (P) : $\Delta n = +1$, $\Delta S > 0$. ΔH is negative.

$\Delta G = \Delta H - T\Delta S$ is negative at all temperatures, i.e., process is spontaneous at all temperatures.

(Q) : The process is exothermic, i.e., ΔH is negative. Also $\Delta S < 0$. ΔG would be negative at low temperature.

(R) : $\Delta H = +ve$; $\Delta n = +2$, so $\Delta S > 0$. Hence, ΔG would be negative at high temperature.

(S) : $\Delta H = +ve$; $\Delta n = -1$, so $\Delta S < 0$. Hence, ΔG would be positive at all temperatures.

35. (c) : At high pressure all the gases have $Z > 1$ and are difficult to compress.

36. (b) : In case of endothermic reactions, ΔG will be negative when $|\Delta H| < |T\Delta S|$. To increase the magnitude of $T\Delta S$, the temperature (T) should be increased. Thus, endothermic reactions

can be made spontaneous by increasing the temperature. Therefore, a reaction which is non-spontaneous at low temperature becomes spontaneous at high temperature and *vice versa*.

37. (a) : a' is measure of magnitude of intermolecular attractive forces.

38. (a) : The process of dissolution is usually endothermic, i.e., $\Delta_{\text{sol}}H^\circ > 0$, the solubility should increase with rise in temperature.

39. (a)

40. (d) : During the free expansion of a gas in vacuum $P_{\text{ex}} = 0$. Hence, no work is done whether the process is reversible or irreversible.

41. (3) : According to Dalton's law, $P = P'_A + P'_B$
 $1.5 = 1.0 + P'_B \Rightarrow P'_B = 0.5 \text{ atm}$

$$\text{For gas A, } P'_A \times V = \frac{2}{M_A} RT$$

$$\text{For gas B, } P'_B \times V = \frac{3}{M_B} RT$$

$$\frac{P'_A}{P'_B} = \frac{2}{3} \times \frac{M_B}{M_A} \Rightarrow \frac{M_B}{M_A} = \frac{3}{2} \times \frac{P'_A}{P'_B}$$

$$\frac{M_B}{M_A} = \frac{3}{2} \times \frac{1.0}{0.5} = 3$$

42. (3) : $\Delta U = q + w = (-1 \text{ kJ}) + 4 \text{ kJ} = +3 \text{ kJ}$

43. (9) : Molar ratio of He and CH_4 is 4 : 1.
 Partial pressure ratio of He and CH_4 is

$$20 \times \frac{4}{5} : 20 \times \frac{1}{5} = 16 : 4$$

$$\begin{aligned} \frac{n_{\text{He}}}{n_{\text{CH}_4}} &= \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} \times \frac{P_{\text{He}}}{P_{\text{CH}_4}} \\ &= \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8 : 1 \end{aligned}$$

$$\therefore x = 8; y = 1 \Rightarrow x + y = 8 + 1 = 9$$

44. (3) : $\Delta H = \Delta U + \Delta n_g RT$;

$$\Delta n_g = n_{g(\text{products})} - n_{g(\text{reactants})} = 0 - 3 = -3$$

$$\therefore \Delta H = \Delta U - 3RT \Rightarrow x = 3$$

45. (3) : $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
 $1 - x \qquad \qquad 2x$

$$\begin{aligned} \text{Total no. of moles } (n_2) &= 1 - x + 2x \\ &= 1 + x = 1.50 \end{aligned}$$

$$(\because x = 50/100 = 0.50)$$

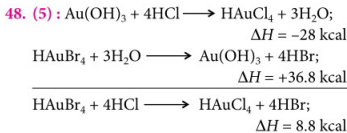
Since the volume of the system remains constant, so

$$\frac{P_1}{n_1 T_1} = \frac{P_2}{n_2 T_2}$$

$$\therefore P_2 = \frac{n_2 T_2}{n_1 T_1} \times P_1 = \frac{1.50 \times 600}{1 \times 300} \times 1 = 3.00 \text{ atm}$$

$$\begin{aligned} 46. (6) : \frac{1}{2} \text{H}_{2(g)} + \frac{1}{2} \text{Cl}_{2(g)} &\rightarrow \text{HCl}_{(g)} \\ \Delta S^\circ &= \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) \\ &= S^\circ_{\text{HCl}} - \left(\frac{1}{2} S^\circ_{\text{H}_2} + \frac{1}{2} S^\circ_{\text{Cl}_2} \right) = 183 - \frac{1}{2} (131 + 223) \\ &= 6 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$47. (2) : \frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \sqrt{\frac{16}{4}} = 2$$



$$\begin{aligned} \therefore \text{Fraction of HAuCl}_4 &= \frac{0.44}{8.8} = 0.05 = 5 \times 10^{-2} \\ \Rightarrow x &= 5 \end{aligned}$$

$$\begin{aligned} 49. (5) : u_{\text{rms}} \text{ of } \text{C}_2\text{H}_6 &= \sqrt{\frac{3RT}{M}} \\ M &= 30; T = 27 + 273 = 300 \text{ K} \end{aligned}$$

$$u_{\text{rms}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{30}}$$

$$\begin{aligned} u_{\text{rms}} &= 4.99 \times 10^4 \text{ cm/sec} \approx 5 \times 10^4 \text{ cm/sec} \\ \Rightarrow x &= 5 \end{aligned}$$

$$\begin{aligned} 50. (2) : \Delta G^\circ &= \Delta G_f^\circ(\text{Ag}^+) + \Delta G_f^\circ(\text{Cl}^-) - \Delta G_f^\circ(\text{AgCl}) \\ &= 77.1 + (-131.2) - (-109.4) = 55.3 \text{ kJ} \\ \Delta G^\circ &= -2.303 RT \log K \end{aligned}$$

$$\log K = -\frac{\Delta G^\circ}{2.303 RT} = -\frac{-55.3 \times 10^3}{2.303 \times 8.314 \times 298} = -9.7$$

$$\begin{aligned} K &= K_{sp} = 1.99 \times 10^{-10} \approx 2 \times 10^{-10} \\ \Rightarrow x &= 2 \end{aligned}$$





CONCEPT BOOSTER

Dear students!! Hope you have checked the pattern of the question papers this year for different competitive examinations. One thing was common, all were based on a grass root conceptual level on that particular topic. Specially, you may have seen in JEE Advanced that mechanism based questions were very much there. This is why please keep your concept on any topic strong and while practising, clock yourself. This article will help you to build the conceptual area on Carboxylic Acids and their Derivatives.

*Arunava Sarkar

Carboxylic acids have the general formula RCOOH and the functional group is $-\text{COOH}$ i.e. carboxyl group. Few of the reactions of aldehydes, ketones and alcohols are reflected in carboxylic acids as

$-\text{C}(=\text{O})-\text{OH}$ group has both the carbonyl group and the alcoholic group.

Carboxyl
 \downarrow
 has obtained from 'hydroxyl'
 \downarrow
 has obtained from 'carbonyl'

Carboxylic acids are widely found in nature. Higher members of carboxylic acids belonging to the

aliphatic family and containing 12-16 carbon atoms are found in nature in the form of glycerol, triesters i.e. fat or oil. This is why these are named as fatty acids. There are natural saturated as well as natural unsaturated fatty acids. Few are named as:

Formula of the natural saturated fatty acids	Common name	Melting point
$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	Lauric acid	45°C
$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Palmitic acid	63°C
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Stearic acid	69°C
$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	Arachidic acid	76°C

Formula of the natural unsaturated fatty acids	Common name	Melting point
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Palmitoleic acid	0°C
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Oleic acid	13°C
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Linoleic acid	-4.88°C
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Linolenic acid	-10°C
All are Z isomers.		

Lower saturated aliphatic acids (containing 4-10 carbon atoms) have unpleasant odours and they have low melting point. Fatty acids are important components of the biomolecules called *lipids*.

Nomenclature of Carboxylic Acids

Broadly, carboxylic acids are classified into two major categories:

- **Aliphatic carboxylic acids** : Here, the $-\text{COOH}$ group is attached with hydrogen atom or the alkyl group ($-\text{R}$). i.e. HCOOH or RCOOH .
- **Aromatic carboxylic acids** : Here, the $-\text{COOH}$ group is attached to the aryl group ($-\text{Ar}$) i.e. ArCOOH .

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

Based on the number of -COOH groups present in one molecule of the carboxylic acid, it can be classified as monocarboxylic acid, dicarboxylic acid or tricarboxylic acid and so on.

ALIPHATIC CARBOXYLIC ACIDS

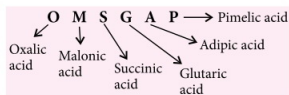
Nomenclature of Monocarboxylic Acids

Common name : Common names of the aliphatic monocarboxylic acids are generally given as per their sources. For example:

Formula of the carboxylic acids	Common name	Sources
HCOOH	Formic acid	Ant (in Latin ' <i>formica</i> ' means ant)
CH_3COOH	Acetic acid	Vinegar (Latin ' <i>acetum</i> ')
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Milk (Greek origin ' <i>protus prion</i> ')
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	Butyric acid	Butter (Latin ' <i>butyrum</i> ')
$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	Valeric acid	Valerian root
$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Caproic acid	Goats (Latin ' <i>caper</i> ')
$\text{CH}_3(\text{CH}_2)_5\text{COOH}$	Enanthic acid	Vines (Greek ' <i>oenanthe</i> ')
$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	Caprylic acid	Goats (Latin ' <i>caper</i> ')
$\text{CH}_3(\text{CH}_2)_7\text{COOH}$	Pelargonic acid	Pelargonium herbs
$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	Capric acid	Goats (Latin ' <i>caper</i> ')

Nomenclature of Dicarboxylic Acids

For dicarboxylic acids, those which have systematic origin are named by their sources whereas some may not have systematic origin and are named following some other conventions. Among many dicarboxylic acids, the most important acids can be remembered using the following techniques:



Now, English alphabet 'O' looks like zero. Therefore, in case of oxalic acid in between two -COOH groups, there is zero carbon group present. After this, for every successive alphabet, value will increase by 'one', i.e.

O → assigned '0' → zero $\text{-CH}_2\text{-}$ group in between two -COOH groups
M → assigned '1' → one $\text{-CH}_2\text{-}$ group in between two -COOH groups
S → assigned '2' → two $\text{-CH}_2\text{-}$ groups in between two -COOH groups

G → assigned '3' → three $\text{-CH}_2\text{-}$ groups in between two -COOH groups
A → assigned '4' → four $\text{-CH}_2\text{-}$ groups in between two -COOH groups
P → assigned '5' → five $\text{-CH}_2\text{-}$ groups in between two -COOH groups

So, Oxalic acid is $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$

Malonic acid is $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \\ | \\ \text{COOH} \end{array}$

Succinic acid is $\begin{array}{c} \text{COOH} \\ | \\ (\text{CH}_2)_2 \\ | \\ \text{COOH} \end{array}$ and so on.

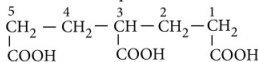
Nomenclature of Tricarboxylic Acids

Here, the IUPAC format is much more used than the common system.

Methodology for naming the tricarboxylic acids:

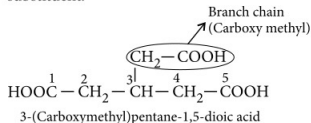
○ If all the three -COOH groups are attached

with the parent chain then the —COOH groups are not included in the parent chain and the acid is named as the derivative of the parent alkane. For example:



Pentane-1,3,5-tricarboxylic acid

- If all the three —COOH groups are not directly attached to the parent alkane then two suitable —COOH groups are included in the parent chain and the third one is considered to be a substituent.



AROMATIC CARBOXYLIC ACIDS

Nomenclature of Monocarboxylic Acids

Aromatic monocarboxylic acids are named as the derivative of the parent acid *i.e.* the benzoic acid $\text{C}_6\text{H}_5\text{—COOH}$. Few of them also have common names. For example,

	<i>o</i> -Hydroxybenzoic acid or 2-Hydroxybenzoic acid (IUPAC) or Salicylic acid (Common name)
	<i>o</i> -Aminobenzoic acid or 2-Aminobenzoic acid (IUPAC) or Anthranilic acid (Common name)
	<i>p</i> -Methoxybenzoic acid or 4-Methoxybenzoic acid (IUPAC) or <i>p</i> -Anisic acid (Common name)
	<i>p</i> -Methylbenzoic acid or 4-Methylbenzoic acid (IUPAC) or <i>p</i> -Toluic acid (Common name)

In every case, the carbon atom (of the ring) which is directly attached to the benzene ring is given position 1.

Nomenclature of Dicarboxylic Acids

Aromatic dicarboxylic acids are also named in usual manner. Few common examples are :

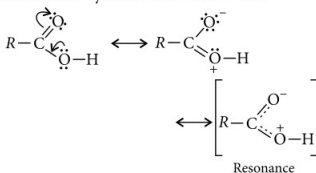
	Benzene-1,2-dicarboxylic acid (IUPAC) or Phthalic acid (Common name)
	Benzene-1,3-dicarboxylic acid (IUPAC) or Isophthalic acid (Common name)
	Benzene-1,4-dicarboxylic acid (IUPAC) or Terephthalic acid (Common name)

Structure of Carboxyl Group and Its Resonance

Different spectrochemical studies suggest that —COOH group has planar structure. Here, the carbon atom and both the oxygen atoms are sp^2 -hybridised. Now, there are few facts which confirm the resonance hybrid structure of carboxyl group (carboxylic acid). These are

- Normally, carbon-oxygen single bond length is 143 pm. But the carbon-oxygen single bond length in case of carboxylic acid is found to be shorter than that. It is 136 pm.
- Normally, carbon-oxygen double bond length in carboxylic acid is a little bit longer than that. It is 123 pm.

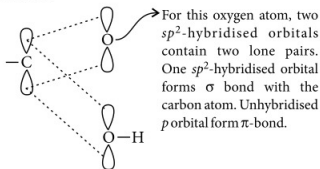
From these data, it can be said that carboxylic acid has a resonance hybrid structure as follows:



So, the π -bond is delocalised in between the carbon atom and two oxygen atoms.

This is why the bonding structure in carboxyl group is as follows:

Carbon atom uses its two sp^2 -hybridised orbitals out of three sp^2 -hybridised orbitals to get overlapped with two oxygen atoms where both the oxygen atoms use their sp^2 -hybrid orbitals. The unhybridised p orbitals of carbon and two oxygen atoms are parallel to each other and can form a π -bond which is partially delocalised in between those three. The π -bond formation can be shown as below:



Carboxyl carbon is less electropositive and hence less electrophilic due to the +R effect of the $-\text{OH}$ group. Thus carboxyl carbon is less electrophilic than carbonyl carbon which has following two resonating structures:



Physical Properties of Carboxylic Acids

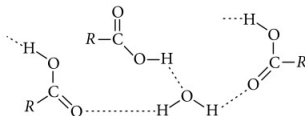
Carboxylic acids have some important physical properties as :

- **Odour** : Aliphatic acids have different types of smell based on the number of carbon atoms present. Aliphatic acids with C_1-C_3 have pungent smell, C_4-C_9 have a kind of foul smell. From C_1-C_9 , aliphatic acids are comparatively more volatile whereas aliphatic acids with carbon number > 10 do not have any characteristic smell due to low volatility.
- **Physical state** : Aliphatic acids with carbon number, C_1-C_3 are liquids, C_4-C_9 are oily liquids and $> \text{C}_{10}$ are waxy solids.
- **Colour** : Almost all carboxylic acids in pure state are colourless.

- **Solubility** : As far as the solubility of a carboxylic acid is concerned, a carboxylic acid can be represented as shown below:

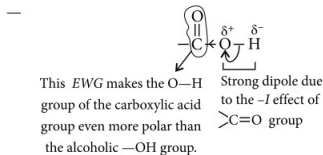


For C_1-C_4 , hydrophobic nature of $-\text{R}$ group is not that dominating as the hydrophilic nature of $-\text{COOH}$ group and hydrogen bonding with molecules of water is present. This is why aliphatic acids with carbon number C_1-C_4 are fairly soluble in water but with carbon number > 5 , hydrophobic nature of the $-\text{R}$ group increases and solubility decreases. In general, aliphatic or aromatic both carboxylic acids are fairly soluble in less polar solvents i.e. aprotic solvents. Aromatic carboxylic acids are very less soluble or almost insoluble in water. Benzoic acid is sufficiently soluble in hot water and sparingly soluble in cold water.

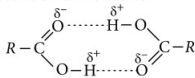


Hydrogen bonding between water and carboxylic acid molecules

- **Boiling point** : In general, among compounds of comparable molecular mass like aldehydes, ketones, alcohols, hydrocarbons and carboxylic acids, it is found that carboxylic acids have higher boiling point. Carboxylic acids can form very strong intermolecular H-bonding than the others. Reasons behind this can be :



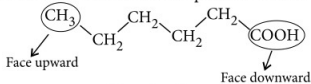
- Intermolecular hydrogen bonding leads to the formation of cyclic dimer through the association of molecules.



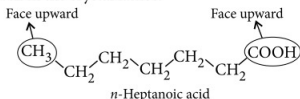
Dimerisation is more prominent in aprotic solvents than in protic solvents as in protic solvent, the solvent molecule forms H-bonding with the acid molecule obstructing the dimer formation. The H-bond which exists in between two carboxylic acid molecules is so strong that it exists in the vapour phase. However, extent of H-bonding is very impressive in case of solid and liquid state.

- Melting point** : Melting point depends on the lattice energy of the crystal lattice. Aliphatic carboxylic acids with carbon number > 10 have high melting point due to high molecular mass which helps in the formation of strong crystal lattice. For example, decanoic acid has the melting point of 31.0°C.

For carbon number, C_1 – C_{10} , alternation effect is observed i.e. carboxylic acid with even number of carbon atoms is having the higher melting point than that of the next aliphatic carboxylic acid containing odd number of carbon atoms. This can be explained as below:



Due to the presence of $-CH_3$ and $-COOH$ groups at the terminal positions with their face directions opposite to each other they can fit well in the crystal lattice.



Here, $-CH_3$ as well as $-COOH$ group has the upward face directions. They cannot fit well in the crystal lattice and thus melting point is relatively low.

n -Hexanoic acid \Rightarrow Melting point = -4.0°C

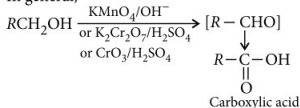
n -Heptanoic acid \Rightarrow Melting point = -7.5°C

Aliphatic carboxylic acids have zig-zag structure, aromatic carboxylic acids have planar structure and hence they can pack very well in the crystal lattice. This is why aromatic carboxylic acids have higher melting point than that of the aliphatic carboxylic acids.

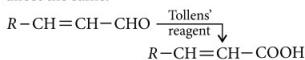
General Methods of Preparation of Aliphatic and Aromatic Carboxylic Acids

- From alcohols and aldehydes** : 1° alcohols are oxidised to carboxylic acids *via* aldehydes. Oxidising agents can be neutral, acidic or basic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7/\text{conc. H}_2\text{SO}_4$ or $\text{CrO}_3/\text{H}_2\text{SO}_4$, etc.

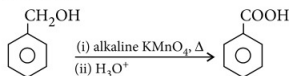
In general,



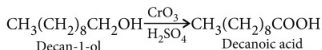
Directly aldehydes can be converted to acids either by any of the above mentioned reagents or by using any mild oxidising agent like Tollens' reagent, Fehling's solution, etc. The advantage of using mild oxidising agent is that it does not affect any carbon-carbon double or triple bond. However, strong oxidising agents affect the same.



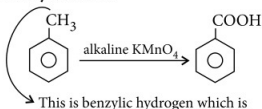
Alkaline KMnO_4 can be used to convert aromatic alcohols to corresponding carboxylic acids. e.g.,



The reagent $\text{CrO}_3/\text{H}_2\text{SO}_4$ is also known as Jones' reagent. It can easily convert the long chain alcohol to the corresponding carboxylic acid.

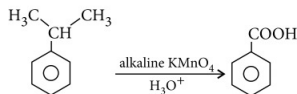
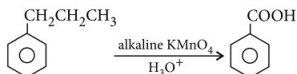
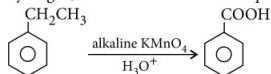


From alkylbenzene :

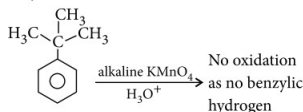


This is benzylic hydrogen which is very prone to oxidation.

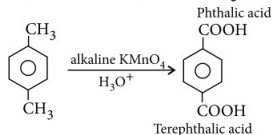
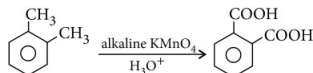
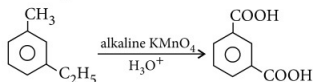
This carbon when oxidised gives $-\text{COOH}$ group irrespective of the length of the alkyl group. But if there is no benzylic hydrogen, then oxidation will not be possible.



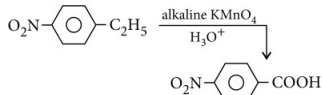
But,



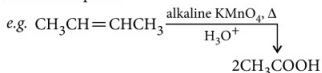
Similarly,



Electron withdrawing groups increase the reactivity of benzylic hydrogen while electron donating groups decrease the same.

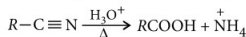


From alkene : Strong oxidising agents convert the alkenes into the corresponding carboxylic acids. Here, rupture of carbon-carbon double bond takes place.



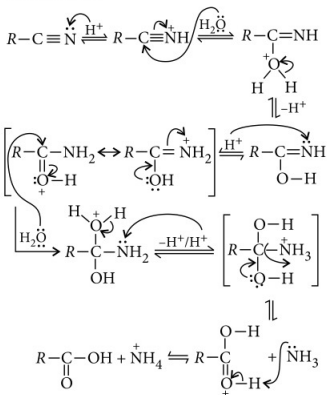
From alkyl nitriles : Alkyl nitriles, either by acid catalysed hydrolysis or by base catalysed hydrolysis gets converted into the corresponding carboxylic acids.

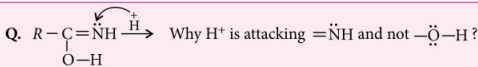
Acid catalysed hydrolysis of alkyl nitriles :



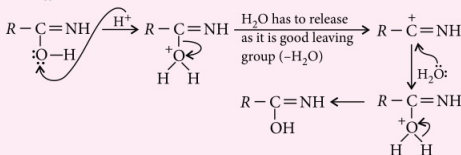
In this reaction NH_4^+ salt is the side product and not the ammonia.

Mechanism :





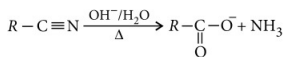
Soln.: If H^+ attacks $-\ddot{\text{O}}-\text{H}$, the same compound is formed back as shown below:



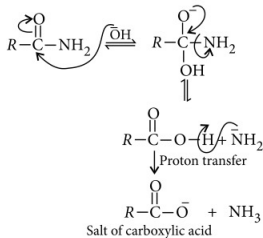
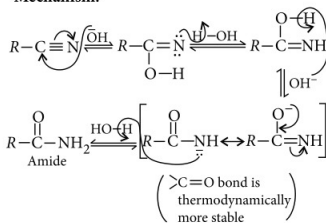
Hence, there is no stable fate for $R-\overset{+}{\text{C}}=\text{NH}$ and it is not possible thermodynamically.

But, if H^+ will attack $=\ddot{\text{N}}\text{H}$ then ultimately it reaches to a stable product. Thermodynamically, the whole phenomenon is possible as it forms RCOOH and NH_4^+ .

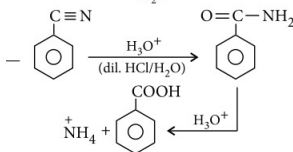
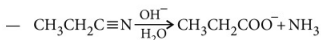
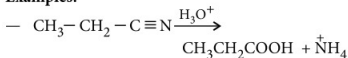
Base catalysed hydrolysis of alkyl nitriles :



Mechanism:



Examples:



From alkyl isonitriles : $R-\text{N}^+\equiv\text{C}^-$ is alkyl isonitrile. This can be acid-hydrolysed but the acid formed is always formic acid (HCOOH).

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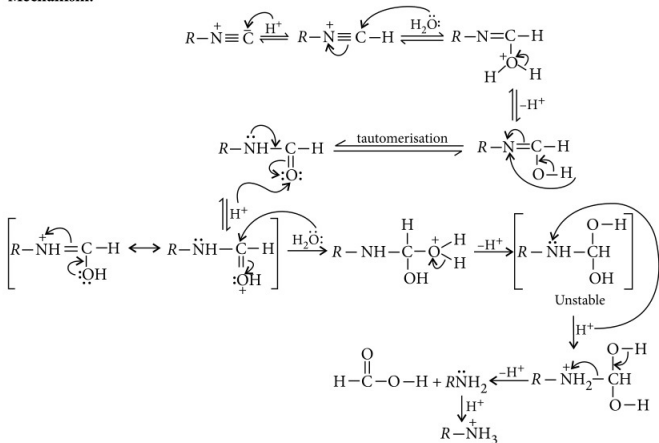
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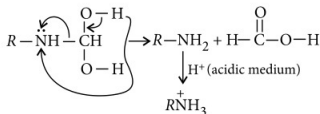
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Mechanism:



The last step could have also been shown as :



Now, the question is whether alkyl isonitriles can be hydrolysed through base or not? The structure of the alkyl isonitrile is

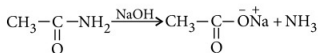


It is completely satisfied with its filled octet and has no vacant d -orbital to accommodate extra electrons.

Here OH^- cannot attack due to the -ve charge on the carbon atom.

This is why alkyl isonitriles cannot be hydrolysed by base.

❑ From acid amide ($RCONH_2$)



From Grignard reagent and carbon dioxide :

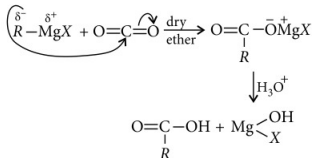
Reactants : (i) Grignard reagent ($RMgX$)

(ii) Carbon dioxide (CO_2)

Here, either CO_2 can be blown (bubbled CO_2) in the ethereal solution of Grignard reagent or in the ethereal suspension of dry ice, Grignard reagent solution may be added.

Product : Addition product is obtained first which on further acidification gives carboxylic acid.

Mechanism:

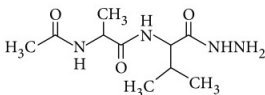


...To be continued on the next issue.

PRACTICE PROBLEMS 2015

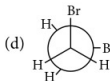
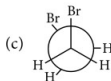
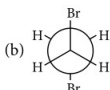
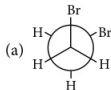
Chemistry Olympiad

1. The number of peptide bonds in the compound



is/are

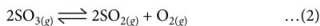
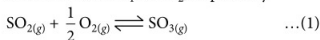
- (a) 1 (b) 2
(c) 3 (d) 4
2. Formula of tear gas is
(a) COCl_2 (b) CCl_3NO_2
(c) N_2O (d) none of these.
3. Which one of the following statement is incorrect?
(a) Frenkel defect does not affect the density of the crystal.
(b) Schottky defect results in the decrease of density of the crystal.
(c) NaCl exhibits only schottky defect.
(d) AgBr exhibits only frenkel defect.
4. In pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, number of σ - and $d\pi$ - $p\pi$ bonds, respectively are
(a) 8 and 2 (b) 6 and 2
(c) 12 and 0 (d) 12 and 2
5. The most stable conformation of 2, 3-dibromobutane is



6. The reaction $A \xrightleftharpoons[k_2]{k_1} C$ follows a 1st order kinetics.

The rate constant for the formation of C is k_1 and that for D is k_2 . The reaction is started with only A . The concentration of C is always equal to the concentration of D at any time. At what time will all the three concentrations be equal?

- (a) $\frac{1}{2k_1} \ln 2$ (b) $\frac{1}{2k_2} \ln 2$
(c) $\frac{1}{2k_1} \ln 3 = \frac{1}{2k_2} \ln 3$ (d) $\frac{1}{k_1 + k_2} \ln 2$
7. Element X has 2 valence electrons, and element Y has 5 valence electrons. The most likely type and formula of the compound formed when X and Y combine chemically are
(a) covalent, X_3Y_2 (b) ionic, X_3Y_2
(c) ionic, X_2Y_3 (d) ionic, X_5Y_2
8. Among the following, the species that is both tetrahedral and diamagnetic is
(a) $[\text{NiCl}_4]^{2-}$ (b) $[\text{Ni}(\text{CO})_4]$
(c) $[\text{Ni}(\text{CN})_4]^{2-}$ (d) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
9. Consider the equilibria (1) and (2) with equilibrium constants K_1 and K_2 , respectively.



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K_1 and K_2 are related as

- (a) $2K_1 = K_2^2$ (b) $K_1^2 = \frac{1}{K_2}$
 (c) $K_2^2 = \frac{1}{K_1}$ (d) $K_2 = \frac{2}{K_1^2}$

10. The weight percent of sucrose (Formula weight = 342 g mol^{-1}) in an aqueous solution is 3.42. The density of the solution is 1 g mL^{-1} , the concentration of sucrose in the solution in mol L^{-1} is

- (a) 0.01 (b) 0.1
 (c) 1.0 (d) 10

11. A compound with molecular formula $\text{C}_4\text{H}_4\text{O}$ has all the four carbon atoms and the oxygen atom in the ring. It also has two double bonds. The compound is

- (a) homocyclic and aromatic
 (b) heterocyclic and aromatic
 (c) homocyclic but not aromatic
 (d) heterocyclic but not aromatic.





12. N_2 and O_2 are converted into monocations N_2^+ and O_2^+ respectively. Which of the following statements is wrong?

- (a) In N_2^+ , N—N bond weakens.
 (b) In O_2^+ , O—O bond order increases.
 (c) In O_2^+ , paramagnetism decreases.
 (d) N_2^+ becomes diamagnetic.

13. The triad of nuclei that is isotonic is

- (a) $^{14}_6\text{C}$, $^{15}_7\text{N}$, $^{17}_9\text{F}$ (b) $^{12}_6\text{C}$, $^{14}_7\text{N}$, $^{19}_9\text{F}$
 (c) $^{14}_6\text{C}$, $^{14}_7\text{N}$, $^{17}_9\text{F}$ (d) $^{14}_6\text{C}$, $^{14}_7\text{N}$, $^{19}_9\text{F}$

14. Compound 'X' on heating with Zn dust gives compound 'Y' which on treatment with O_3 followed by reaction with Zn dust gives propionaldehyde. The structure of 'X' is

- (a)  (b) 
 (c)  (d) 

15. What molar concentration of NH_3 provides a $[\text{OH}^-]$ of 1.5×10^{-3} ?

(Given: K_b of NH_3 is 1.8×10^{-5})

- (a) 0.13 M (b) 0.125 M
 (c) 0.110 M (d) 0.145 M

16. In Kjeldahl's method, the gas evolved from 1.325 g sample of a fertilizer is passed into 50.0 mL of 0.2030 N H_2SO_4 . 25.32 mL of 0.1980 N NaOH are required for the titration of unused acid. Calculate the percentage of nitrogen in fertilizer.

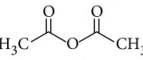
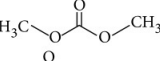
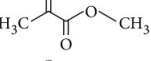
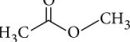
- (a) 5.43% (b) 0.543%
 (c) 54.3% (d) 5.043%

17. The number of sp^2 hybridized carbon atoms in

$\text{HC}\equiv\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}=\text{CH}_2$, are

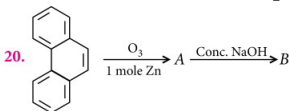
- (a) 3 (b) 5
 (c) 4 (d) 6

18. Which of the following is an anhydride?

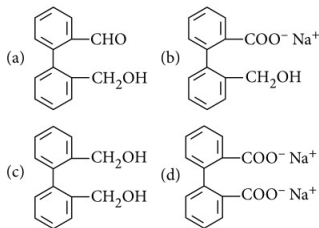
- (a) 
 (b) 
 (c) 
 (d) 

19. During the transformation of $^b_a\text{X} \longrightarrow ^d_c\text{Y}$, the no. of β -particles emitted is

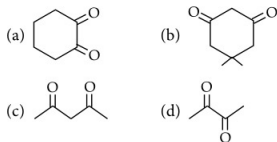
- (a) $(c-a) + \frac{1}{2}(b-d)$ (b) $(a-c) - \frac{1}{2}(b-d)$
 (c) $(b-d) + 2(c-a)$ (d) $(b-d) + \frac{1}{2}(c-a)$



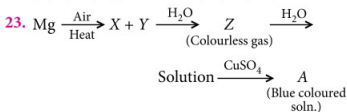
The end product(B) in the above reaction is



21. Which of the following compounds will have least percentage of enol content ?



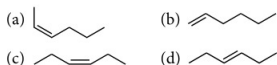
22. The atomic numbers of other elements which lie in the same group as the tenth element in the periodic table are
- (a) 18, 32, 54, 86 (b) 8, 18, 36, 84
(c) 2, 18, 30, 36 (d) 2, 18, 36, 54



Substances X, Y, Z and A respectively are

- (a) Mg_3N_2 , MgO , NH_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (b) $\text{Mg}(\text{NO}_3)_2$, MgO , H_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (c) MgO , Mg_3N_2 , NH_3 , $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (d) $\text{Mg}(\text{NO}_3)_2$, MgO_2 , H_2O_2 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
24. Newspaper contains a toxic material called
- (a) cadmium (b) lead
(c) manganese (d) mercury.

25. The structure of *cis*-3-hexene is



26. Ethyl acetate reacts with $\text{NH}_2\text{NHCONH}_2$ to form
- (a) $\text{CH}_3\text{CONHCONHNH}_2$
 (b) $\text{CH}_3\text{CON}(\text{NH}_2)\text{CONH}_2$
 (c) $\text{CH}_3\text{CONHNHCONH}_2$
 (d) $\text{CH}_3\text{CH}_2\text{NHNHCONH}_2$

27. Among the following, the species with the highest bond order is

- (a) O_2 (b) F_2
(c) O_2^+ (d) F_2^-

28. A specific volume of H_2 requires 24 s to diffuse out of a container. The time required by an equal volume of O_2 to diffuse out under identical conditions, is

- (a) 24 s (b) 96 s
(c) 384 s (d) 192 s

29. The ionization enthalpy of sodium is 495 kJ mol^{-1} . How much energy in Joules must be required to convert all the atoms of sodium to sodium ions present in 2.3 mg of sodium vapours ?

- (a) 495 kJ (b) 49.5 J
(c) 49.5 kJ (d) 4.95 kJ

30. Tailing of mercury can be used as test for which of the following gas ?

- (a) Dioxygen (b) Dihydrogen
(c) Ozone (d) Dinitrogen

ANSWER KEY

1. (a) 2. (b) 3. (d) 4. (d) 5. (b)
 6. (c) 7. (b) 8. (b) 9. (b) 10. (b)
 11. (b) 12. (d) 13. (a) 14. (c) 15. (a)
 16. (a) 17. (a) 18. (a) 19. (a) 20. (b)
 21. (d) 22. (d) 23. (c) 24. (b) 25. (c)
 26. (c) 27. (c) 28. (b) 29. (b) 30. (c)

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UNIT-2 Chemical Thermodynamics | Solutions | Equilibrium

CHEMICAL THERMODYNAMICS

- Introduction
- Fundamentals of Thermodynamics
- System and Surroundings
- Extensive and Intensive Properties
- State Functions
- Thermodynamic Processes
- First law of Thermodynamics
- Work, Heat, Internal Energy and Enthalpy
- Heat Capacity and Molar Heat Capacity
- Hess's Law
- Second Law of Thermodynamics
- Gibbs Free Energy
- Entropy
- Spontaneity

TIPS TO REMEMBER

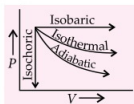
- ❑ **Thermodynamics**: The branch of science which deals with all changes in energy or transfers of energy that accompany physical and chemical processes.
- ❑ **Chemical thermodynamics**: The branch of thermodynamics which deals with the study of processes in which chemical energy is involved.
- ❑ **Thermodynamic terms**
 - **System**: Specified part of the universe or specified portion of the matter which is

under experimental investigation is called system.

- **Isolated system**: Neither matter nor energy is exchanged with the surroundings.
- **Open system**: Both matter and energy are exchanged with the surroundings.
- **Closed system**: Only energy is exchanged with the surroundings.
- **Homogeneous system**: Uniform throughout, one phase only. Physical properties and chemical composition are identical throughout.
- **Heterogeneous system**: Non-uniform, two or more phases. Physical and chemical properties are different.
- **Surroundings**: The rest of the universe which is not the part of the system is called surroundings.
- **Boundary**: Anything that separates system and surroundings is called boundary. It may be rigid or non rigid.
 - **Diathermic boundary**: Conductor of heat.
 - **Adiabatic boundary**: Non-conductor of heat.
- ❑ **Thermodynamic properties**
 - **Extensive properties**: The properties whose magnitude depends upon the quantity of matter present in the system

are called extensive properties. *e.g.*, mass, volume, internal energy, enthalpy, heat capacity, etc.

- **Intensive properties** : The properties which do not depend upon the quantity of matter present in the system or size of the system are called intensive properties. *e.g.*, temperature, density, pressure, refractive index etc.
- **State variables** : Fundamental properties which determine the state of a system are known as state variables. *e.g.*, pressure, volume, temperature, etc.
- **State functions** : The properties which depend upon initial and final states of the system and are independent of the path followed are known as state functions. *e.g.*, enthalpy, entropy, free energy.
 - State variables such as temperature, pressure and volume are also state functions.
- **Thermodynamic process** : An operation that brings about the change in the state of the system is known as thermodynamic process. Various thermodynamic processes are :
 - **Isothermal process** : $dT = 0$ *i.e.*, heat is exchanged with the surroundings and system is not thermally isolated.
 - **Isobaric process** : $dP = 0$ *i.e.*, pressure remains constant throughout the change.
 - **Isochoric process** : $dV = 0$ *i.e.*, volume remains constant.
 - **Adiabatic process** : $dq = 0$ *i.e.*, no exchange of heat between system and surroundings. System is thermally isolated.
 - **Cyclic process** : $dU = 0$; $dH = 0$; when a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.
 - **Reversible process** : Process occurs infinitesimally slowly *i.e.*, opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process.
 - **Irreversible process** : Process goes from initial to final state in a single step in finite time and cannot be reversed.



- **Internal energy** : When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system.
 - It is the sum of different types of energies associated with atoms and molecules such as electronic energy, nuclear energy, chemical bond energy, potential energy and kinetic energy, which is further the sum of translational energy, vibrational energy and rotational energy.
 - In thermodynamics, we call it the internal energy, U of the system, which may change, when
 - heat passes in or out of the system.
 - work is done on or by the system.
 - matter enters or leaves the system.
- **Internal energy change**
 - For chemical reactions, the change in internal energy may be considered as the difference between the internal energies of the products and that of the reactants, *i.e.*, $\Delta U = U_{\text{products}} - U_{\text{reactants}} = U_p - U_r$
 - If the internal energy of the products is less than the internal energy of the reactants, then ΔU would be negative. $\Delta U = U_p - U_r = -ve$ ($\because U_p < U_r$)
 - If the internal energy of the products is more than the internal energy of the reactants, then ΔU would be positive. $\Delta U = U_p - U_r = +ve$ ($\because U_p > U_r$)
- **Heat** : The quantity of energy which flows between a system and its surroundings on account of temperature difference.
 - Heat always flows from high temperature to low temperature.
 - Heat absorbed or evolved, $q = ms\Delta t$ where, m = mass of substance, s = specific heat and Δt = temperature difference.

- **Work**: The mode of energy transfer to or from a system with reference to the surroundings.
 - If an object is displaced through a distance dx against a force F , then the amount of work done is defined as: $W = F \times dx$

Key Points

- Energy transfer as work done on the system, $w > 0$ (+ve), U increases.
- Energy transfer as work done by the system, $w < 0$ (-ve), U decreases.
- Heat flowing into the system, (endothermic) $q > 0$ (+ve), U increases.
- Heat flowing out of the system, (exothermic) $q < 0$ (-ve), U decreases.
- For isothermal expansion of an ideal gas

$$W_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$$

$$\text{or } -2.303nRT \log \frac{P_1}{P_2}$$

$$W_{\text{irrev}} = -P_{\text{ext}} \Delta V$$

$$W_{\text{rev}} > W_{\text{irrev}}$$

- SI unit of heat is joule (J).
 - 1 joule = 0.2390 cal
 - 1 calorie = 4.184 J
 - 1 kcal = 4.184 kJ
 - 1 litre-atm = 101.31 J
- $$= 1.013 \times 10^9 \text{ ergs} = 24.206 \text{ cal}$$

Zeroth Law of Thermodynamics

- "If two bodies are separately in thermal equilibrium with a third system, then they are in thermal equilibrium with each other".

First Law of Thermodynamics

- The first law of thermodynamics is essentially the law of conservation of energy applied to thermodynamic systems. According to this law:
 - Energy can neither be created nor destroyed but it can be converted from one form to another.
 - The total energy of universe is constant.
 - The mass and energy of an isolated system remains constant.
 - The total energy of a system and its surroundings must remain constant, although it may be changed from one form to other.

- Consider a system in state A , having internal energy U_A .
 q amount of heat is supplied to the system so that the system attains the state B , having internal energy U_B . Then change in internal energy $\Delta U = U_B - U_A$. Let w is the work done on the system to attain this change, then from first law of thermodynamics heat absorbed by the system = Increase in its internal energy – work done on the system

$$\therefore q = \Delta U - w$$

$$\text{or } \Delta U = q + w \quad \dots(i)$$

Equation (i) represents the mathematical statement of first law of thermodynamics.

- Also for an infinitesimal change

$$dU = dq + dw$$

In case q is the heat absorbed and w the work done by the system, then the relationship becomes

$$\Delta U = q + (-w) = q - w$$

"The increase in the internal energy of a thermodynamic system is equal to the amount of heat energy added to the system minus the work done by the system on the surroundings."

Enthalpy

- Heat content of a system at constant pressure is called enthalpy, denoted by ' H '.

From first law of thermodynamics;

$$q = U + PV \quad \dots(i)$$

Heat change at constant pressure can be given as

$$\Delta q = \Delta U + P\Delta V \quad \dots(ii)$$

At constant pressure heat can be replaced by enthalpy,

$$\Delta H = \Delta U + P\Delta V \quad \dots(iii)$$

At constant volume, $\Delta V = 0$; thus, equation (ii) can be written as $\Delta q = \Delta U$

$\therefore \Delta H$ = Heat change or heat of reaction at constant pressure

ΔU = Heat change or heat of reaction at constant volume.

- In case of solids and liquids participating in a reaction,

$$\Delta H \approx \Delta U \quad (P\Delta V \approx 0)$$

- Difference between ΔH and ΔU is significant when gases are involved in a chemical reaction.

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = \Delta U + \Delta nRT \quad (\because P\Delta V = \Delta nRT)$$

Δn = Number of gaseous moles of products – Number of gaseous moles of reactants

- Enthalpy of the elements is taken as zero at standard states.

Heat Capacity (C) and Molar Heat Capacity (C_m)

- The heat capacity of a system is the amount of heat needed to raise the temperature of the given substance by one degree celsius (or one kelvin). Thus, if temperature of a substance changes from t_1 to t_2 then the heat required will be $q = C\Delta t$
where, Δt = change in temperature ($t_2 - t_1$). Heat capacity is directly proportional to the amount of the substance.
- The molar heat capacity of a substance is its heat capacity for one mole of substance.

$$C_m = \frac{C}{n}$$

- The heat capacity at constant volume

$$\Delta V = 0$$

$$\therefore P\Delta V = 0; W = 0$$

$$\therefore q = \Delta U$$

$$\text{Therefore } C_V = \left(\frac{\Delta U}{\Delta T} \right)_V$$

- The heat capacity at constant pressure

$$q = \Delta U - W$$

$$\text{and } C_P = \left(\frac{dq}{dT} \right)_P$$

As there is an increase in volume, work is done by the system i.e., W is negative and hence,

$$W = -P\Delta V$$

$$\text{Thus, } q = \Delta U - W$$

$$= \Delta U - (-P\Delta V) = \Delta U + P\Delta V$$

$$\text{but } \Delta U + P\Delta V = \Delta H$$

On replacing this value in the equation.

$$C_P = \left(\frac{dq}{dT} \right)_P \text{ we get}$$

$$C_P = \left(\frac{\Delta H}{\Delta T} \right)_P$$

Therefore, "molar heat capacity at constant volume is defined as the increase in internal energy of system per degree rise of temperature" whereas, "molar heat capacity at constant pressure is defined as the increase in enthalpy of the system per degree rise of temperature".

- **Relation between C_P and C_V** : The two heat capacities are not equal, but C_P is greater than C_V .

At constant volume, heat absorbed

$$q_V = C_V \Delta T = \Delta U$$

At constant pressure, heat absorbed

$$q_P = C_P \Delta T = \Delta H$$

The difference between C_P and C_V can be derived from an ideal gas as

$$\text{for one mole of an ideal gas, } \Delta H = \Delta U + P\Delta V$$

$$\text{or } \Delta H = \Delta U + \Delta(RT) = \Delta U + R\Delta T$$

$$\therefore \Delta H = \Delta U + R\Delta T \text{ for one mole of an ideal gas.}$$

Substituting the values of ΔH and ΔU ,

$$C_P \Delta T = C_V \Delta T + R\Delta T$$

$$\text{or } C_P = C_V + R$$

$$\therefore C_P - C_V = R \text{ (for one mole of an ideal gas.)}$$

Similarly, for n moles of an ideal gas,

$$C_P - C_V = nR$$

Nature of the gas	Monatomic (He, Ar)	Diatomic (H_2 , O_2 , CO)	Triatomic (CO_2 , H_2S)
$\gamma = \frac{C_P}{C_V}$	$\frac{(5/2)R}{(3/2)R}$ $= \frac{5}{3} = 1.66$	$\frac{(7/2)R}{(5/2)R}$ $= \frac{7}{5} = 1.40$	$\frac{4R}{3R}$ $= \frac{4}{3} = 1.33$

- Let n_1 and n_2 moles of two non-reacting gases A and B are mixed, heat capacity of the mixture may be calculated as

$$(C_V)_{\text{mixture}} = \frac{n_1(C_V)_1 + n_2(C_V)_2}{n_1 + n_2}$$

Enthalpy Changes for Some Reactions

- **Enthalpy of reaction** : The heat change or the amount of heat evolved or absorbed when the number of moles of reactants react completely to give the products as given by the balanced chemical equation,

$$\Delta H = \sum a_i H_{(\text{products})} - \sum b_i H_{(\text{reactants})}$$

where a_i and b_i represent the coefficients of the products and reactants respectively.

- **Enthalpy of formation** : The enthalpy change when one mole of a substance is formed directly from its constituent elements.
- **Enthalpy of combustion** : The enthalpy change when one mole of a substance is completely burnt in oxygen.

- ❑ **Enthalpy of neutralisation** : The enthalpy change when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in dilute solutions.
- ❑ **Enthalpy of fusion** : The enthalpy change when one mole of a solid substance is completely converted into liquid state at its melting point.
- ❑ **Enthalpy of vaporisation** : The enthalpy change when one mole of the substance from liquid state is completely converted into its vapours at its boiling point.
- ❑ **Enthalpy of sublimation** : The enthalpy change when one mole of a solid is directly converted into vapours.
- ❑ **Enthalpy of atomization** : The change in enthalpy when one mole of a substance dissociates into gaseous atoms.
- ❑ **Enthalpy of ionisation** : The change in enthalpy when one mole of a covalent compound on dissolution in water splits to produce ions in the solution.
- ❑ **Enthalpy of hydration** : The enthalpy change when one mole of the anhydrous salt combines with the required number of moles of water so as to change into the hydrated salt.
- ❑ **Enthalpy of solution** : The change in enthalpy when one mole of a substance is dissolved in a given amount of the solvent.
 - If solvent is taken in excess so that no further heat is evolved on dilution, it is called enthalpy of solution at infinite dilution.

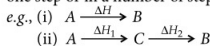
$$\Delta_{\text{sol}}H = \Delta_{\text{lattice}}H + \Delta_{\text{hyd}}H$$
 - Lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of the ionic compound dissociates into ions in the gaseous state.

$$\Delta_{\text{lattice}}H$$
 is calculated using Born-Haber's cycle,

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2}D + IP - EA + LE$$
 where, Q = heat of formation,
 D = dissociation energy,
 IP = ionization potential,
 EA = electron affinity,
 LE = lattice energy.

Hess's Law of Constant Heat Summation

- ❑ It states that the enthalpy change (or heat evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.



According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2$

Kirchhoff's Equation

- ❑ It gives influence of temperature on the heat of reaction.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P \quad (\text{at constant } P)$$

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V \quad (\text{at constant } V)$$

Bond Enthalpy

- ❑ The amount of energy released when one mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous molecules.

$$\Delta H = \sum B.E._{(\text{reactants})} - \sum B.E._{(\text{products})}$$

- ❑ Bond fission is an endothermic process whereas bond formation is an exothermic process.
- ❑ In case of diatomic molecules, bond enthalpy is equal to bond dissociation enthalpy.
- ❑ Bond enthalpy is the same as the enthalpy of atomization for all diatomic molecules.
- ❑ Average (mean) bond enthalpy is the total enthalpy of atomization of the molecule divided by the number of bonds.
- ❑ Bond enthalpy usually means bond dissociation enthalpy. Hence, it is always taken as positive because it is the energy required and not the energy released. Further, it is the energy for one mole of a particular type of bonds and not for one mole of the substance.

Entropy

- ❑ It is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system. It is denoted by 'S'.
 - Order of randomness or disorder

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

- The driving force for a spontaneous process is an increase in the entropy of the universe.

□ **Entropy change** : It is defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\int dS = \frac{1}{T} \int dq_{rev} \Rightarrow \Delta S = \frac{q_{rev}}{T}$$

- $\Delta S > 0$ (increase in entropy) when heat is absorbed.
- $\Delta S < 0$ (decrease in entropy) when heat is evolved.
- Entropy change for a reaction,
 $\Delta_r S = S_{(\text{products})} - S_{(\text{reactants})}$
- Entropy change of an ideal gas (for one mole),

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} = C_P \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

- At constant temperature (isothermal process),

$$\Delta S_T = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

- At constant volume (isochoric process),

$$\Delta S_V = C_V \ln \frac{T_2}{T_1} = C_V \ln \frac{P_2}{P_1}$$

- At constant pressure (isobaric process),

$$\Delta S_P = C_P \ln \frac{T_2}{T_1} = C_P \ln \frac{V_2}{V_1}$$

Second Law of Thermodynamics

- “The entropy of the universe is continuously increasing” or “Heat cannot flow of its own from colder to hotter region.”
- For reversible processes :
 $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$
- For irreversible processes :
 $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$

Entropy Change and Spontaneity

- For a spontaneous process,
 ΔS_{total} or $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$
 Here, ΔS_{total} is also called $\Delta S_{universe}$.
- At equilibrium, $\Delta S = 0$ (for an isolated system).
- ΔS is $-ve$ i.e., $\Delta S < 0$; direct process is non-spontaneous whereas reverse process is spontaneous.

Gibbs Free Energy

- The thermodynamic quantity of the system, decrease in whose value during a process is equal to useful work done by the system.

- Mathematically, it may be defined as

$$G = H - TS \quad \dots(i)$$

where, H = enthalpy; S = entropy and
 T = absolute temperature

We know that, $H = U + PV$... (ii)

From eqns.(i) and (ii),

$$G = U + PV - TS$$

Free energy change at constant temperature and pressure can be given as

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

$$\Delta G = \Delta H - T\Delta S \quad \dots(iii)$$

(Gibbs-Helmholtz equation)

$$(\because \Delta H = \Delta U + P\Delta V)$$

Gibbs Free Energy Change and Spontaneity

- Gibbs-Helmholtz equation is used to discuss the driving force, i.e., the overall criterion of spontaneity.

ΔH	ΔS	ΔG	Remarks
-ve	+ve	-ve	Spontaneous at all temperatures.
		-ve (at low temperature)	Spontaneous
-ve	-ve	+ve (at high temperature)	Non-spontaneous
		+ve (at low temperature)	Non-spontaneous
+ve	+ve	-ve (at high temperature)	Spontaneous
+ve	-ve	+ve	Non-spontaneous at all temperatures.

Key Points

- Entropy changes during phase transitions :

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}, \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}, \Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}$$

- $\Delta_r G^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$

- For an isothermal and isobaric process :

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{sys} = -T\Delta S_{total}$$

- $\Delta G^\circ = -2.303 RT \log K_{eq} = -nFE^\circ_{cell}$

- For elementary substances, $G_f^\circ = 0$

Third Law of Thermodynamics

- "Entropy of a perfectly crystalline solid is zero at absolute zero."
- Crystals of CO, N₂O, NO and H₂O do not have zero entropy even at absolute zero.

SOLUTIONS

- Introduction
- Types of solution
- Different Methods for Expressing Concentration of Solution
- Solubility and Henry's Law
- Vapour Pressure of Solutions and Raoult's Law
- Ideal and Non-ideal Solutions
- Colligative Properties of Dilute Solutions
- van't Hoff factor

TIPS TO REMEMBER

- **Solution** : A homogeneous mixture of two or more components of variable composition is termed as a solution.
- **Solvent** : The component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists.
- **Solute** : One or more components present in the solution other than solvent are called solutes which are present in lesser proportions.
- **Binary solution** : It is composed of two components solute and solvent.
- **Dilute solution** : A solution in which relatively a small amount of the solute is present is called a dilute solution.
- **Concentrated solution** : A solution in which relatively a large amount of the solute is present is called a concentrated solution.
- **Saturated solution** : A solution which contains the maximum amount of the solute that can be dissolved in a given amount of the solvent at a particular temperature is called a saturated solution.
- **Supersaturated solution** : A solution in which amount of solute is more than it can dissolve at a particular temperature is called supersaturated solution.

Types of Solution

- Solution may be prepared by any combination of three states of matter (solids, liquids and gases).
 - Solutions may be of nine types depending upon the states of the solvent and the solute.

Type of solution	Solute	Solvent	Common examples
Gaseous solutions	Gas	Gas	Mixture of oxygen and nitrogen gases.
	Liquid	Gas	Chloroform mixed with nitrogen gas.
	Solid	Gas	Camphor in nitrogen gas.
Liquid solutions	Gas	Liquid	Oxygen dissolved in water.
	Liquid	Liquid	Ethanol dissolved in water.
	Solid	Liquid	Glucose dissolved in water.
Solid solutions	Gas	Solid	Solution of hydrogen in palladium.
	Liquid	Solid	Amalgam of mercury with sodium.
	Solid	Solid	Copper dissolved in gold, alloys.

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Different Methods for Expressing Concentration of Solutions

Name	Symbol	Formula	Definition	Effect of temperature
Mass percentage	% (w/W)	$\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$	Amount of solute in grams present in 100 g of solution.	No effect
Mass by volume percentage	% (w/V)	$\frac{\text{Mass of solute}}{\text{Total volume of solution in mL}} \times 100$	Amount of solute in grams dissolved in 100 mL of the solution.	Changes with change of temperature.
Volume percentage	% (v/V)	$\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$	Volume of solute in mL dissolved in 100 mL of the solution.	Changes with change of temperature.
Strength	$\frac{\text{g/L}}{(\text{or g/dm}^3)}$	$\frac{\text{Mass of solute in grams}}{\text{Volume of solution in L /dm}^3}$	Amount of solute in grams present in one litre (or dm^3) of solution.	Changes with change of temperature.
Parts per million	ppm	$\frac{\text{No. of parts of solute}}{\text{Total no. of parts of all components of solution}} \times 10^6$	Number of parts of solute present in million (10^6) parts of solution.	No effect
Mole fraction	x	$x_A = \frac{n_A}{n_A + n_B}, x_B = \frac{n_B}{n_A + n_B}$ $x_A + x_B = 1$	Ratio of number of moles of one component to the total number of moles of all the components.	No effect
Molarity	M	$\frac{\text{Moles of solute}}{\text{Volume of solution in L /dm}^3}$	Number of moles of solute dissolved one litre (or one dm^3) of solution.	Changes with change of temperature.
Molality	m	$\frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$	Number of moles of solute per 1 kg of the solvent.	No effect
Normality	N	$\frac{\text{No. of gram equivalents of solute}}{\text{Volume of solution in L}}$	Number of gram equivalents of the solute dissolved per litre (dm^3) of the solution.	Changes with change of temperature.
Formality	F	$\frac{\text{Gram formula mass of solute}}{\text{Volume of solution in L}}$	Number of gram formula masses of the solute dissolved per litre of solution.	Changes with change of temperature.

Key Points

- ❑ Molarity of dilution, $M_1V_1 = M_2V_2$
- ❑ Molarity of mixing,

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$
 where M_R = Resultant molarity,
 $V_1 + V_2 + V_3$ = Resultant volume after mixing
- ❑ Equivalents of acids and bases : Mass that donates or accepts a mole of proton.
- ❑ Equivalents of oxidizing and reducing agents : Mass that provides or accepts a mole of electrons.
- ❑ Unit of normality is gram equivalents litre⁻¹.
- ❑ When a solution is diluted x times, its normality also decreases by x times.
- ❑ Relation between normality and molarity,

$$\text{Normality} = \frac{\text{Mol. mass}}{\text{Eq. mass}} \times \text{Molarity}$$

$$\text{Normality} = n \times \text{Molarity}$$
- ❑ In case formula mass is equal to the molecular mass, the formality and molarity are the same.

- ❑ **Solubility** of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- ❑ **Factors affecting solubility of a solid in a liquid**
 - **Nature of solute and solvent** : Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents. (*i.e.*, like dissolves like).
 - **Effect of temperature** :
 - If the dissolution process is endothermic ($\Delta_{\text{sol}}H > 0$), the solubility increases with rise in temperature.
 - If dissolution process is exothermic ($\Delta_{\text{sol}}H < 0$) the solubility decreases with rise in temperature.

- **Effect of pressure** : Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.

❑ Factors affecting solubility of a gas in a liquid

- **Effect of pressure** : Henry's law states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution".
 $p = K_H x$ where, K_H is the Henry's law constant and is different for different gases at a particular temperature.
 Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid.
- **Effect of temperature** : As dissolution is an exothermic process, then according to Le Chatelier's Principle, the solubility should decrease with increase of temperature.

Vapour Pressure of Solutions and Raoult's Law

❑ Vapour pressure of liquid-liquid solutions

- **Raoult's law** : It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.
 For component 1, $p_1 = p_1^\circ x_1$
 For component 2, $p_2 = p_2^\circ x_2$
- According to Dalton's law of partial pressures,

$$p_{\text{total}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ = p_1^\circ + (p_2^\circ - p_1^\circ) x_2$$
 where p_1°, p_2° are vapour pressures of pure components 1 and 2 respectively.
- If y_i is the mole fraction of the any component i in the vapour phase, then

$$p_i = y_i p_{\text{total}}$$
- Raoult's law is special case of Henry's law in which K_H becomes equal to p_i° .

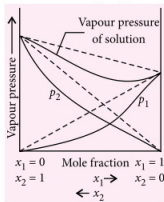
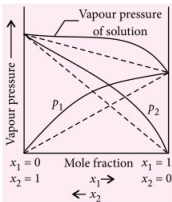
- ❑ **Vapour pressure of solutions of solids in liquids** : Vapour pressure of the solution at a given temperature is lower than the vapour pressure of the pure solvent at the same temperature.

Ideal and Non-ideal Solutions

Ideal solutions	Non-ideal solutions
Obeys Raoult's law at all temperatures and concentrations.	Do not obey Raoult's law at all temperatures and concentrations.
$p_1 = x_1 p_1^\circ; p_2 = x_2 p_2^\circ$	$p_1 \neq x_1 p_1^\circ; p_2 \neq x_2 p_2^\circ$
$\Delta H_{\text{mix}} = 0, \Delta V_{\text{mix}} = 0$	$\Delta H_{\text{mix}} \neq 0, \Delta V_{\text{mix}} \neq 0$
A - B interactions \approx A - A and B - B interactions	A - B interactions \neq A - A and B - B interactions.
Do not form azeotropes (constant boiling mixtures).	Form azeotropes.

Non-ideal Solutions showing Positive and Negative Deviations from Raoult's Law

Solutions showing positive deviation	Solutions showing negative deviation
A - B $<$ A - A or B - B interactions	A - B $>$ A - A or B - B interactions.
$\Delta H_{\text{mix}} > 0, \Delta V_{\text{mix}} > 0$	$\Delta H_{\text{mix}} < 0, \Delta V_{\text{mix}} < 0$
$p_i > p_i^\circ x_i$	$p_i < p_i^\circ x_i$
Form minimum boiling azeotropes.	Form maximum boiling azeotropes.
Examples: Ethanol and acetone, Carbon disulphide and acetone, Methanol and water, Cyclohexanol and cyclohexane.	Examples: Phenol and aniline, Chloroform and acetone, Chloroform and diethyl ether, Chloroform and benzene, Water and H_2SO_4 or HNO_3 or HCl.



Azeotropes

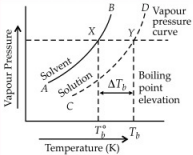
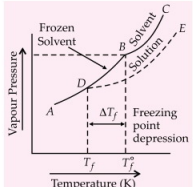
- Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation.
- There are two types of azeotropes called minimum boiling azeotropes and maximum boiling azeotropes.
 - The solutions which show a large positive deviation from Raoult's law form minimum

boiling azeotropes at a specific composition. e.g., ethanol-water mixture.

- The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. e.g., nitric acid-water mixture.

Colligative Properties of Dilute Solutions

- Colligative properties are the properties which depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution.

Colligative properties	Expression
<p>Relative lowering of vapour pressure : When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution is lower than that of the pure solvent. It is known as lowering of vapour pressure and relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.</p>	$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B = \frac{n_B}{n_A + n_B}$ $= \frac{n_B}{n_A} = \frac{W_B \times M_A}{M_B \times W_A}$ <p>(\because for dilute solutions, $n_B \ll n_A$)</p>
<p>Elevation in boiling point: The boiling point of a solution containing non-volatile solute is always higher than boiling point of pure solvent. This increase in boiling point is termed as elevation in boiling point.</p>	 $\Delta T_b = T_b - T_b^\circ$ $\Delta T_b \propto m \text{ or } \Delta T_b = K_b m = K_b \left(\frac{W_B \times 1000}{M_B \times W_A} \right)$ <p>or $M_B = \frac{1000 \times W_B \times K_b}{\Delta T_b \times W_A}$</p> <p>$K_b$ is called boiling point elevation constant or molal elevation constant or Ebullioscopic constant, having unit $K \text{ kg mol}^{-1}$.</p>
<p>Depression in freezing point: The freezing point of a solution containing non-volatile solute is always less than the freezing point of a pure solvent. The decrease in freezing point is termed as depression in freezing point.</p>	 $\Delta T_f = T_f^\circ - T_f$ $\Delta T_f \propto m$ <p>or $\Delta T_f = K_f m = K_f \left(\frac{W_B \times 1000}{M_B \times W_A} \right)$</p> <p>or $M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$</p> <p>$K_f$ is known as freezing point depression constant or molal depression constant or Cryoscopic constant, having unit $K \text{ kg mol}^{-1}$.</p>
<p>Osmosis and osmotic Pressure : When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. The movement of solvent molecules from less concentrated solution to more concentrated solution through semipermeable membrane is termed as osmosis. The hydrostatic pressure which develops on account of osmosis is called osmotic pressure or the excess pressure that must be applied on the solution to prevent osmosis is called osmotic pressure.</p>	$\pi = CRT = \left(\frac{n_B}{V} \right) RT,$ $\pi V = \frac{W_B RT}{M_B}$ <p>or $M_B = \frac{W_B RT}{\pi V}$</p>

Reverse Osmosis

- If external pressure greater than osmotic pressure is applied on the solution, the flow of solvent molecules can be made to proceed from solution towards pure solvent, *i.e.*, in reverse direction of the ordinary osmosis. This is termed as reverse osmosis.

Isotonic Solutions

- Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

Hypotonic Solution

- If one solution is of lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution.

Hypertonic Solution

- The more concentrated solution is said to be hypertonic with respect to the dilute solution.

Abnormal Molar Mass

- For substances undergoing association or dissociation in solution, the molecular mass determined by studying any of the colligative properties is different than the theoretically expected value, and the substance is said to show abnormal molecular mass.

van't Hoff Factor (*i*)

- It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

$$i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{\text{Total number of moles of particles after association / dissociation}}{\text{Number of moles of particles before association / dissociation}}$$

- For association, $i < 1$; For dissociation, $i > 1$
- Relation between van't Hoff factor and degree of dissociation, $\alpha = \frac{i-1}{n-1}$

- Relation between van't Hoff factor and degree of association, $\alpha = \frac{1-i}{1-1/n}$

Modified equations for colligative properties

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i \cdot \frac{n_B}{n_A}$$

$$\Delta T_b = iK_b m, \Delta T_f = iK_f m, \pi = i n_B RT/V$$

EQUILIBRIUM

- Introduction
- Equilibria Involving Physical Processes
- Equilibria Involving Chemical Processes
- Ionic Equilibrium

TIPS TO REMEMBER

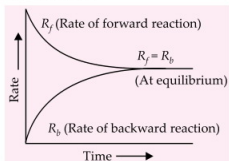
Physical Equilibrium

- Opposing processes involve physical changes.
- Phase transformation processes
 - Solid-Liquid equilibrium :
 $r_{\text{Melting of ice}} = r_{\text{Freezing of water}}$
 - Liquid-Gas equilibrium :
 $r_{\text{Evaporation}} = r_{\text{Condensation}}$
 - Solid-Gas equilibrium :
 $r_{\text{Sublimation}} = r_{\text{Condensation}}$
 - Solid-Solution equilibrium :
 $r_{\text{Dissolution}} = r_{\text{Precipitation}}$
 - Gas-Solution equilibrium :
 $m \propto p$ [Henry's law]

Chemical Equilibrium

- Opposing processes involve chemical changes.
- Irreversible reactions : Chemical reactions in which reactants are completely converted into products and reactions which move only in forward direction are known as irreversible reactions. *e.g.*,
 $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$
- Reversible reactions : Chemical reactions which take place in both directions under similar conditions are known as reversible reactions. *e.g.*,
 $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$
- Equilibrium state : It is the stage of the reversible reaction at which the concentration

of the reactants and products do not change with time *i.e.*, a stage comes when the rate of forward reaction becomes equal to rate of backward reaction, this stage is called equilibrium state.



- ❑ **Dynamic equilibrium:** In chemical equilibrium both forward and backward reactions do not stop but proceed at equal rates, and the concentrations of reactants and products remain constant. Therefore, equilibrium is dynamic in nature.

❑ Characteristics of chemical equilibrium

- Equilibrium state is reached only if process is carried out in a closed vessel.
- At equilibrium, concentrations of the reactants and products remain constant.
- At equilibrium, rate of forward reaction = rate of backward reaction and equilibrium is dynamic in nature.
- Chemical equilibrium can be attained from either direction.
- A catalyst does not alter the state of equilibrium. It simply helps to attain the equilibrium quickly.

❑ Types of chemical equilibrium

- **Homogeneous equilibrium :** All the reactants and products are in the same phase. *e.g.*,

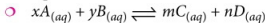
$$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$$
- **Heterogeneous equilibrium :** Reactants and products are in two or more different phases. *e.g.*,

$$\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{(g)} + \text{H}_{2(g)}$$

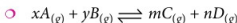
❑ Law of chemical equilibrium and equilibrium constant

- At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical

equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the equilibrium law or law of chemical equilibrium.



$$K_c = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$



$$K_p = \frac{(p_C)^m (p_D)^n}{(p_A)^x (p_B)^y}$$

❑ Relation between K_p and K_c

- $K_p = K_c (RT)^{\Delta n}$
 where $\Delta n = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$
 - If $\Delta n = 0$, $K_p = K_c$
 - If $\Delta n = +ve$, $K_p > K_c$
 - If $\Delta n = -ve$, $K_p < K_c$

❑ Characteristics of equilibrium constant

- Independent of initial concentration or volume of reactants.
- Not influenced by the presence of catalyst.
- Dependent on temperature but independent of the direction of attainment of equilibrium:
 - For endothermic reactions, the equilibrium constant increases (k_f increases more than k_b) with rise in temperature and decreases with decrease in temperature.
 - For exothermic reactions, equilibrium constant decreases (k_b increases more than k_f) with rise in temperature and increases with fall in temperature.
 - The variation of equilibrium constant with temperature is given by van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where

K_1 = equilibrium constant at temperature T_1 ,
 K_2 = equilibrium constant at temperature T_2 ,
 ΔH = heat of reaction (enthalpy change)

- Independent of addition of inert material to the system.
- Dependent on stoichiometry of reactants and products at equilibrium:
 - If reaction is reversed, equilibrium constant is inverted i.e., $K' = 1/K$.
 - If equation for a reaction is divided by a factor of 'n', the new equilibrium constant becomes n^{th} root of the previous equilibrium constant.
i.e., $K' = \sqrt[n]{K}$
 - If equation for a reaction is multiplied by a factor 'n' then the new equilibrium constant (K') becomes equal to K^n .
i.e., $K' = K^n$
 - If equation is written in a number of steps, then its equilibrium constant will be multiple of equilibrium constants of each step.
i.e., $K = K_1 \times K_2 \times K_3 \times \dots K_n$

❑ **Units of equilibrium constant :** The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

- Equilibrium constants can also be expressed as dimensionless quantities if the standard states of reactants and products are specified.

❑ **Relation between Gibbs free energy and equilibrium constant**

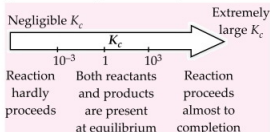
- At equilibrium,
 $\Delta G^\circ = -RT \ln K$; $K = e^{-\Delta G^\circ/RT}$
 - If $\Delta G^\circ < 0$ then $K > 1$
[Forward reaction is favoured.]
 - If $\Delta G^\circ > 0$ then $K < 1$
[Reversed reaction is favoured.]
 - If $\Delta G^\circ = 0$, then $K = 1$
[Reaction is in equilibrium.]

❑ **Applications of equilibrium constant**

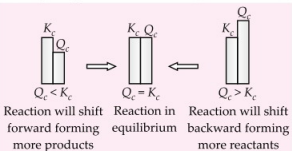
- Value of equilibrium constant of a reversible reaction is a measure of the tendency of the reaction to go in the forward reaction.

Greater the value of equilibrium constant, greater will be tendency of the reaction to proceed in forward direction.

- The value of equilibrium constant also indicates the thermodynamic stability of the products. Greater the equilibrium constant of a reaction, greater will be the stability of the products and unstability of the reactants.
- Equilibrium constant is required for the calculation of equilibrium concentrations of reactants as well as products.
- Predicting the extent of reaction :
 - $K_c > 10^3$ [Forward reaction is favoured.]
 - $K_c < 10^{-3}$ [Reverse reaction is favoured.]
 - $10^{-3} < K_c < 10^3$ [Both reactants and products are present in equilibrium.]



- Predicting the direction of reaction :
 - $Q_c > K_c$ [Reverse reaction is favoured.]
 - $Q_c < K_c$ [Forward reaction is favoured.]
 - $Q_c = K_c$ [Reaction is in equilibrium.]



Factors Affecting Equilibrium

- Le Chatelier's principle :** If a system in equilibrium is subjected to change of concentration, pressure or temperature, equilibrium shifts in the direction that tends to undo the change imposed.
- Effect of change in concentration :** Increase in concentration of reactants favours forward reaction and increase in concentration of products favours backward reaction.

- **Effect of change in temperature :** High temperature favours endothermic reactions and low temperature favours exothermic reactions.
- **Effect of change in pressure :** High pressure favours the direction in which lesser number of moles of the gas are produced and low pressure favours the direction in which larger number of moles of the gas are produced.
- **Effect of inert gas addition :** Addition of inert gas at constant volume does not affect the equilibrium and addition of inert gas at constant pressure favours the direction in which larger number of moles of the gas are produced.
- **Effect of adding catalyst :** The addition of catalyst does not affect the equilibrium.

Ionic Equilibrium

- **Electrolytes:** Substances that conduct electricity in their aqueous solutions or in molten state are called electrolytes.
- **Strong electrolytes :** These electrolytes are almost completely ionised when dissolved in a polar medium like water. In solution they are excellent conductors, e.g., HNO_3 , HCl .
- **Weak electrolytes :** These are not completely ionised when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH_3COOH , H_3PO_4 .

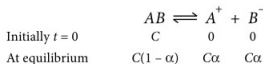
- **Degree of dissociation :** It may be defined as a fraction of total number of molecules of an electrolyte which dissociates into ions.

$$\alpha = \frac{\text{No. of molecules of electrolyte dissociated as ions}}{\text{Total numbers of molecules of electrolyte dissolved}}$$

- For strong electrolytes, $\alpha = 1$.
- For weak electrolytes, $\alpha < 1$.

Ostwald's Dilution Law

- A dynamic equilibrium exists between ions and unionised molecules of the electrolyte in solution.
- Consider a binary electrolyte AB which dissociates into A^+ and B^- ions and the equilibrium state is represented by the equation



So, dissociation constant may be given as

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \dots (i)$$

For very weak electrolytes,

$$\alpha \ll 1, (1-\alpha) \approx 1$$

$$\therefore K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \quad \dots (ii)$$

Concentration of any ion = $C\alpha = \sqrt{CK}$

From equation (ii), it is clear that degree of ionization increases on dilution.

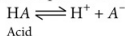
Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

- **Limitations of Ostwald's dilution law :** The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes.
 - The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution.
 - When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium.

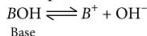
Acids and Bases

Arrhenius concept

- Arrhenius acid furnishes hydrogen (H^+) ions in aqueous solution. e.g., HCl .

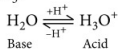


- Arrhenius base furnishes hydroxyl (OH^-) ions in aqueous solution. e.g., NaOH .



Bronsted-Lowry concept

- Bronsted acid donates a proton (H^+). e.g., HCl .
- Bronsted base accepts a proton (H^+). e.g., NH_3 .



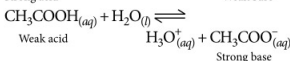
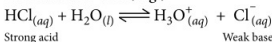
□ Lewis concept

- Lewis base donates a pair of electrons. *e.g.*, NH_3 .
 - Lewis acid accepts a pair of electrons. *e.g.*, BF_3 .
- $$\text{H}^+ + \underset{\text{Acid}}{\text{:}\ddot{\text{O}}\text{:}}\text{H}^- \rightleftharpoons \text{H}:\ddot{\text{O}}:\text{H} \quad \text{Base}$$

□ Conjugate acid - base pair : Conjugate acid-base pair is a pair of acid and base which differs by a proton (H^+), *e.g.*,

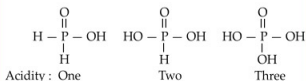
Acid $\xrightleftharpoons{+\text{H}^+}$ Conjugate base

- Relative strengths of conjugate acids and bases depend upon their tendency to donate a proton or to accept a proton.
- Stronger the acid, weaker is its conjugate base and vice versa, *e.g.*,



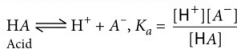
Key Points

- Number of replaceable hydrogen ions in acid is called basicity of the acid and number of replaceable hydroxyl ions in base is called acidity of the base.
- Number of replaceable hydrogen ions in an oxyacid is equal to the number of the hydrogen attached through oxygen to the central atom.

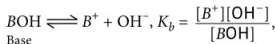


- Substances like HCl , H_2SO_4 , H_3PO_4 capable of losing proton are called protonic acids.
- Substances which can accept as well as donate a proton are called amphiprotic or amphoteric substances *e.g.* HCO_3^- , HSO_4^- , HS^- , H_2O , NH_2 , etc.

□ Ionisation of acids and bases



$$\text{degree of ionisation, } \alpha = \sqrt{\frac{K_a}{C}}$$

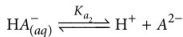
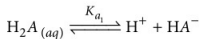


$$\text{Degree of ionisation, } \alpha = \sqrt{\frac{K_b}{C}}$$

Greater the degree of ionisation or greater the dissociation constant (K_a or K_b), stronger is the acid or base.

□ Multistage ionisation of acids and bases

Consider a dibasic acid,

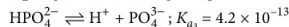
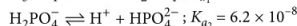
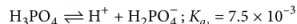


The ionisation constants K_{a_1} and K_{a_2} are given as

$$K_{a_1} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]}, K_{a_2} = \frac{[\text{H}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

$$K_{a_1} > K_{a_2}$$

For example,



$$K_{a_1} > K_{a_2} > K_{a_3}$$

- The reason for decrease in the dissociation constant of successive stages is that in the first dissociation, a neutral molecule gives a proton (H^+), while in the second stage of dissociation, the proton is coming from a negatively charged molecule and in the third step of dissociation, a doubly negatively charged molecule is giving a proton which in turn is more difficult than first two dissociations.
- Similarly for a polyacidic base, $K_{b_1} > K_{b_2} > K_{b_3}$ and so on.

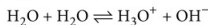
Ionic Product of Water (K_w)

- Ionic product of water is the product of molar concentration of H_3O^+ ions and OH^- ions in pure water or in any acidic or basic solution. It is constant at a particular temperature.

At 298 K,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

In pure water,



$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Thus at 298 K,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mole litre}^{-1}$$

- **Effect of temperature on K_w** : The value of K_w increases with increase of temperature. With increase in temperature, degree of ionisation of water increases, so more of H_2O molecules dissociate into H^+ and OH^- ions and hence ionic product also increases.

pH and Salt Hydrolysis

- pH of a solution is defined as the negative logarithm of hydrogen ion concentration.

$$\text{pH} = -\log[\text{H}^+] \text{ or } \text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{or } \text{pH} = \log \frac{1}{[\text{H}^+]}$$

Similarly, negative logarithm of hydroxyl ion concentration is called pOH.

$$\text{pOH} = -\log[\text{OH}^-] \text{ or } \text{pOH} = \log \frac{1}{[\text{OH}^-]}$$

□ Salt hydrolysis

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline $\text{pH} > 7$	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic $\text{pH} < 7$	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, $\text{pH} = 7$ (If $K_a = K_b$)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

- **pH-scale** : A solution is classified as acidic, basic or neutral based on its pH value.

- If $\text{pH} = \text{pOH} = 7$, then solution will be neutral.
- If $\text{pH} < 7$ or $\text{pOH} > 7$, then solution will be acidic.
- If $\text{pH} > 7$ or $\text{pOH} < 7$, then solution will be basic.

pH scale varies from 0 to 14.

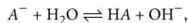
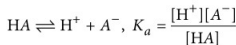
- Relationship between pH and pOH

$$\text{pH} + \text{pOH} = 14$$

and

$$\text{pH} + \text{pOH} = \text{p}K_w$$

- **$\text{p}K_a$ and $\text{p}K_b$** : If K_a and K_b are the dissociation constants of weak acid and weak base respectively then, $\text{p}K_a = -\log K_a$ and $\text{p}K_b = -\log K_b$. Consider a weak acid, HA



$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]}$$

Multiplying K_a and K_b

$$K_a \times K_b = [\text{H}^+][\text{OH}^-]$$

But $[\text{H}^+][\text{OH}^-] = K_w$

$$\therefore K_a \times K_b = K_w$$

Taking log on both sides,

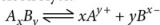
$$\log K_a + \log K_b = \log K_w$$

$$\text{or } -\log K_a - \log K_b = -\log K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

Solubility Product

- It is defined as the product of molar concentrations of ions of an electrolyte in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.



Applying law of mass action,

$$K_{eq} = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_xB_y]}$$

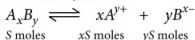
As conc. of $[A_xB_y]$ undissociated is almost constant.

$$K_{eq}[A_xB_y] = [A^{y+}]^x [B^{x-}]^y$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

- Relation between solubility and solubility product**

- If solubility of a sparingly soluble salt, A_xB_y is S mol/litre, then



Thus, $[A^{y+}] = xS$ and $[B^{x-}] = yS$

$$\therefore K_{sp} = [A^{y+}]^x [B^{x-}]^y = (xS)^x (yS)^y \text{ or } x^x y^y S^{(x+y)}$$

Type of salt	Example	Relation between S and K_{sp}
1 : 1 (AB)	$AgCl, BaSO_4$, etc.	$S = \sqrt{K_{sp}}$ or $K_{sp} = S^2$
1 : 2 (AB_2)	$PbCl_2, Ca(OH)_2$, etc.	$S = \sqrt[3]{K_{sp} / 4}$ or $K_{sp} = 4S^3$
2 : 1 (A_2B)	Ag_2CrO_4, Ag_2CO_3 , etc.	$S = \sqrt[3]{K_{sp} / 4}$ or $K_{sp} = 4S^3$
1 : 3 (AB_3)	$Fe(OH)_3, Al(OH)_3$, etc.	$S = \sqrt[4]{K_{sp} / 27}$ or $K_{sp} = 27S^4$

- Criteria of precipitation of an electrolyte**

- $K_{ip} > K_{sp}$, Precipitation occurs.
- $K_{ip} < K_{sp}$, Precipitation does not occur.
- $K_{ip} = K_{sp}$, Solution is saturated.

Common Ion Effect

- The phenomenon of lowering the degree of ionisation of a weak electrolyte by adding a solution of a strong electrolyte having common ion is called common ion effect.

- As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased.
- The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group.

Buffer Solution

- It is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted.

- Buffer solution has a definite pH value at specific temperature.

- Types of buffer solutions**

- Simple buffer** : Solutions of salt of weak acid and weak base. *i.e.*, CH_3COONH_4

- Acidic buffer**

- Solutions of a mixture of weak acid and its salt with strong base.
i.e., $CH_3COOH + CH_3COONa$
- They have $pH < 7$.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

- Basic buffer**

- Solutions of mixture of weak base and its salt with strong acid.
i.e., $NH_4OH + NH_4Cl$
- They have $pH > 7$.

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

- Buffer capacity** : It is the number of moles of an acid or base added to change pH of one litre of buffer solution by one unit.

Hence, Buffer capacity

$$= \frac{\text{Number of moles of acid or base added per litre of buffer}}{\text{Change in pH}} = \frac{dn}{d(pH)}$$

Questions for Practice

1. Which one of the following statements is false?
 - (a) Work is a state function.
 - (b) Temperature is a state function.
 - (c) Change in the state is completely defined when the initial and final states are specified.
 - (d) Work appears at the boundary of the system.
2. Two elements A and B form compounds having molecular formulae AB_2 and AB_4 , when dissolved in 20 g of C_6H_6 , 1.0 g AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. The atomic masses of A and B are, respectively
 - (a) 26, 42.64
 - (b) 31.72, 47.02
 - (c) 13.11, 24.25
 - (d) 19.17, 35.01
3. If S_1 , S_2 , S_3 and S_4 are the solubilities of $AgCl$ in water, in 0.01 M $CaCl_2$, in 0.01 M $NaCl$ and in 0.05 M $AgNO_3$ respectively at a certain temperature, the correct order of solubilities is
 - (a) $S_1 > S_2 > S_3 > S_4$
 - (b) $S_1 > S_3 > S_2 > S_4$
 - (c) $S_1 > S_2 = S_3 > S_4$
 - (d) $S_1 > S_3 > S_4 > S_2$
4. Enthalpy of the reaction,

$$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$$
 is negative. If enthalpy of formation of CH_4 and CH_3OH are x and y respectively, then which relation is correct?
 - (a) $x > y$
 - (b) $x < y$
 - (c) $x = y$
 - (d) $x \geq y$
5. 0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at -0.062°C . Which of the following is the apparent percentage of dissociation? ($K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}$)
 - (a) 25%
 - (b) 50.5%
 - (c) 78.0%
 - (d) 100%
6. An equilibrium is $A + B \rightleftharpoons C + D$. Initially, we start with equal concentration of A and B . At equilibrium, we find that the moles of C is two times of A . What is the equilibrium constant of the reaction?
 - (a) $1/4$
 - (b) 2
 - (c) 4
 - (d) $1/2$
7. For the process

$$H_2O_{(l)} (1 \text{ bar}, 373 \text{ K}) \rightarrow H_2O_{(g)} (1 \text{ bar}, 373 \text{ K}),$$
 the correct set of thermodynamic parameters is
 - (a) $\Delta G = 0, \Delta S = +ve$
 - (b) $\Delta G = 0, \Delta S = -ve$
 - (c) $\Delta G = +ve, \Delta S = 0$
 - (d) $\Delta G = -ve, \Delta S = +ve$.
8. Phenol associates in benzene to a certain extent to form a dimer. A solution containing $2.0 \times 10^{-2} \text{ kg}$ of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. The degree of association of phenol is (K_f for benzene = $5.12 \text{ K kg mol}^{-1}$)
 - (a) 73.4%
 - (b) 50.1%
 - (c) 42.3%
 - (d) 25.1%
9. $CaSO_4$ is precipitated on mixing equal volumes of the following solutions
[Given : K_{sp} of $CaSO_4$ is 4×10^{-12}]
 - (a) $3 \times 10^{-6} \text{ M } CaCl_2$ and $3 \times 10^{-6} \text{ M } (NH_4)_2SO_4$
 - (b) $4 \times 10^{-6} \text{ M } CaCl_2$ and $3 \times 10^{-6} \text{ M } (NH_4)_2SO_4$
 - (c) $6 \times 10^{-6} \text{ M } CaCl_2$ and $3 \times 10^{-6} \text{ M } (NH_4)_2SO_4$
 - (d) $1 \times 10^{-6} \text{ M } CaCl_2$ and $4 \times 10^{-6} \text{ M } (NH_4)_2SO_4$
10. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
 - (a) ΔH is $-ve, \Delta S$ is $+ve$
 - (b) ΔH and ΔS both are $+ve$
 - (c) ΔH and ΔS both are $-ve$
 - (d) ΔH is $+ve, \Delta S$ is $-ve$.
11. The degree of dissociation (α) of a weak electrolyte, A_xB_y , is related to van't Hoff factor (i) by the expression
 - (a) $\alpha = \frac{i-1}{(x+y-1)}$
 - (b) $\alpha = \frac{i-1}{(x+y+1)}$
 - (c) $\alpha = \frac{(x+y-1)}{i-1}$
 - (d) $\alpha = \frac{(x+y+1)}{i-1}$

The p-BLOCK ELEMENTS (Group 13 and 14)

[Last e^- enters into np -orbital]

Group 13 or IIIA : Boron Family

(B, Al, Ga, In, Tl)

Electronic Configuration

[Noble gas] ns^2np^1

Oxidation States

+1 and +3

Metallic Character

B, Al, Ga, In, Tl
Metalloid Metals

Abundance

Al is the most abundant metal and third most abundant element by mass in the Earth's crust.

Physical Properties

- Atomic radii, ionic radii, density and stability of +1 oxidation state increase down the group.
- Electronegativity, boiling point and stability of +3 oxidation state decrease down the group.
- The melting point decreases from B to Ga and then increases.
- IE_1 is lower than the corresponding group 2 elements.
- IE_{II} is higher than the corresponding group 2 elements.
- IE follows the order: $B > Tl > Ga > Al > In$
- Molecules such as BCl_3 , $AlCl_3$ etc. behave as Lewis acids due to incomplete octet.
- They form complexes because of small size, increased charge and availability of vacant d -orbitals.

Chemical Properties

Reactivity towards air:

- They react with oxygen at high temperatures to form trioxides of the formula M_2O_3 .
 - Except Ga, In, Tl other react with dinitrogen at high temperature to form nitrides of the formula MN .
 - Basic character of their oxides and hydroxides increases down the group.
- | | | | | |
|-----------|------------|------------|------------|---------|
| B_2O_3 | Al_2O_3 | Ga_2O_3 | In_2O_3 | Tl_2O |
| or | or | or | or | or |
| $B(OH)_3$ | $Al(OH)_3$ | $Ga(OH)_3$ | $In(OH)_3$ | $TlOH$ |
| Acidic | Amphoteric | | Basic | |

Reactivity towards water:

- B does not react with water or steam. Al reacts with water and forms protective layer of Al_2O_3 .
- Ga and In do not react with cold or hot water.
- Tl forms $TlOH$ in moist air.

Reactivity towards acids:

- B does not react with non-oxidising acids like HCl.
- B reacts with strong oxidising acids at high temperature forming boric acid (H_3BO_3).
- All other elements react with both non-oxidising and oxidising acids, liberating H_2 gas.

Reactivity towards alkalis:

- Above 773 K, B reacts with alkalis forming borates and liberating H_2 gas.
- Al and Ga being amphoteric react with alkalis, liberating H_2 gas.
- In and Tl do not react with alkalis.

Reactivity towards halogens:

- They react with halogens at high temperature forming trihalides of the formula MX_3 except TlI_3 .

Group 14 or IVA: Carbon Family

(C, Si, Ge, Sn, Pb)

Electronic Configuration

[Noble gas] ns^2np^2

Oxidation States

+2 and +4

Metallic Character

C, Si, Ge, Sn, Pb
Non-metal Metalloids Metals

Abundance

C is the seventeenth and Si is the second most abundant element by mass in the Earth's crust.

Chemical Properties

Reactivity towards air:

- They form oxides of the formula MO and MO_2 on heating with air.
 - Acidic strength of their oxides decreases down the group.
- | | | |
|---------------|-------------|----------------|
| CO_2, SiO_2 | GeO_2 | SnO_2, PbO_2 |
| Acidic | Less acidic | Amphoteric |
| CO, SiO | GeO | SnO, PbO |
| Neutral | Acidic | Amphoteric |

Reactivity towards water:

- C, Si and Ge react with water, liberating H_2 gas.
- Pb does not react with water due to protective layer of oxide.

Reactivity towards acids:

- C and Si do not react with non-oxidising acids.
- Ge (metal) forms germanium chloroform ($GeHCl_3$) on heating with HCl.
- Sn reacts slowly with dil. HCl and readily with conc. HCl.
- Pb reacts with dil. HCl.

Reactivity towards alkalis:

- C does not react with alkalis.
- Si reacts slowly with cold alkali and readily with hot alkali.
- Sn and Pb react slowly with cold alkali and readily with hot alkali.

Reactivity towards halogens:

- They form halides of the formula MX_4 and MX_2 .
- Except C, all react directly with halogens.
- Except C and Si, all form dihalides.

Important Compounds of C and Si

Oxides

- CO is poisonous and neutral oxide.
- CO_2 is greenhouse, non-combustible and acidic oxide.
- Used in artificial respiration as 'Carbogen' (95% O_2 + 5% CO_2).

- Silica (SiO_2):** Purest form of silica is quartz or rock crystal.

- Silicones:** Contain repeated R_2SiO units held by Si-O-Si linkages.

- Silicates:** Basic unit is SiO_4^{4-}

- 3D-Silicates:** Zeolites ($NaAlSi_3O_8 \cdot H_2O$)

Anomalous Behaviour of B

Due to small size, high ionisation enthalpy and absence of d -orbitals:

- B is hardest having highest m.pt. and b.pt.
- B shows maximum covalency of 4 while rest show maximum covalency of 6.
- B exhibits allotropy.
- B does not form B^{3+} ions in solution.

Important Compounds of B

Borax

- $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
- It exists in three forms:
 - Prismatic borax: $Na_2B_4O_7 \cdot 10H_2O$ (also called 'Tincal' or 'Subhaga')
 - Octahedral borax: $Na_2B_4O_7 \cdot 5H_2O$ (also called 'Jeweller's borax')
 - Anhydrous borax: $Na_2B_4O_7$ (also called 'borax glass')

Boron hydrides (boranes)

- Nido-boranes: B_nH_{n+4}
- Arachno-boranes: B_nH_{n+6}
- $B_2H_6 + 2NH_3 \xrightarrow{\text{low temp}}$ $B_2H_6 \cdot 2NH_3$
- $3B_2H_6 \cdot 2NH_3 \xrightarrow{473 K}$ $2B_3N_3H_6 + 12H_2$
Borazole (Inorganic benzene)

Structure of diborane (B_2H_6)

- Four 2 centre-2 electron bonds
- Two 3 centre-2 electron bonds (banana bonds)



Boric acid (H_3BO_3 or $B(OH)_3$)

- Lewis acid
- Used as mild antiseptic and eye wash under the name 'boric lotion'.



Anomalous Behaviour of C

Due to small size, high ionisation enthalpy and absence of d -orbitals:

- C is hardest having highest m.pt. and b.pt.
- C shows maximum covalency of 4 while rest show maximum covalency of 6.
- C has maximum tendency for catenation and multiple bonding ($p\pi-p\pi$) and shows allotropy.

12. The exothermic formation of ClF_3 is represented by the equation:



Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3 ?

- Increasing the temperature
 - Removing Cl_2
 - Increasing the volume of the container
 - Adding F_2 .
13. Values of ΔH and ΔS for five different reactions are given below:

Reaction	$\Delta H(\text{kJ mol}^{-1})$	$\Delta S(\text{JK}^{-1} \text{mol}^{-1})$
I	+ 98.0	+ 14.8
II	- 55.5	- 84.8
III	+ 28.3	- 17.0
IV	- 40.5	+ 24.6
V	+ 34.7	0.0

On the basis of these values, predict which one of these will be spontaneous at all temperatures?

- Reaction I
 - Reaction II
 - Reaction III
 - Reaction IV
14. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mole of X and 3 moles of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively
- 200 and 300
 - 300 and 400
 - 400 and 600
 - 500 and 600
15. If $\text{p}K_b$ for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is
- 1.74×10^{-5}
 - 3.52×10^{-3}
 - 6.76×10^{-4}
 - 5.38×10^{-2}
16. The heat of combustion of solid benzoic acid at constant volume is -321.30 kJ at 27°C. The heat of combustion at constant pressure is
- $-321.30 - 300R$
 - $-321.30 + 300R$
 - $-321.30 - 150R$
 - none of these.

17. A solution of $\text{Al}_2(\text{SO}_4)_3$ ($d = 1.253 \text{ g/mL}$) contains 22.0% salt by weight, what is the molarity, normality and molality of the solution.

- 0.805 M, 4.84 N, 0.825 m
- 0.825 M, 48.3 N, 0.805 m
- 4.83 M, 4.83 N, 4.83 m
- None of these.

18. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is

- 1 : 9
- 1 : 36
- 1 : 1
- 1 : 3

19. The enthalpy change involved in the oxidation of glucose is $-2880 \text{ kJ mol}^{-1}$. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk eating 120 g of glucose?

- 7.9 km
- 9.7 km
- 4.8 km
- 8.4 km

20. When 2 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene is raised by 0.88 K. Which of the following may be the solute?

(K_b for benzene = $2.53 \text{ K kg mol}^{-1}$)

- $\text{CO}(\text{NH}_2)_2$
- $\text{C}_6\text{H}_{12}\text{O}_6$
- NaCl
- None of these

21. Two buffers (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA . Both the buffers are 0.50 M in HA . What would be the pH of the solution obtained by mixing equal volumes of two buffers?

($K_{\text{HA}} = 1.0 \times 10^{-5}$)

- 2.6
- 4.1
- 5.7
- 7.3

22. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be (Given : $R = 8.314 \text{ J/mol K}$)

- (a) $q = +208 \text{ J}$, $w = +208 \text{ J}$
 (b) $q = +208 \text{ J}$, $w = -208 \text{ J}$
 (c) $q = -208 \text{ J}$, $w = -208 \text{ J}$
 (d) $q = -208 \text{ J}$, $w = +208 \text{ J}$

23. Which one of the following statements is false?

- (a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction.
 (b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution.
 (c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$.
 (d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression.

24. Sulphanilic acid is a/an

- (a) Arrhenius acid (b) Lewis base
 (c) Neither (a) nor (b) (d) Both (a) and (b).

25. The standard molar heat of formation of ethane, CO_2 and water(l) respectively are -21.0 , -94.1 and -68.3 kcal . The standard molar heat of combustion of ethane will be

- (a) -372 kcal (b) -340 kcal
 (c) 162 kcal (d) 183.5 kcal

26. The boiling point of an azeotropic mixture of water and ethanol is less than that of water and ethanol. The mixture shows

- (a) negative deviation from Raoult's law
 (b) positive deviation from Raoult's law
 (c) no deviation from Raoult's law
 (d) deviation which cannot be predicted from the given information.

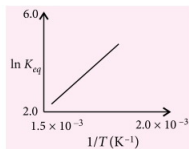
27. For the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, which of the following is the correct statement, if N_2 is added at equilibrium condition?

- (a) The equilibrium will shift to forward direction because according to Π^{nd} law of thermodynamics, the entropy must increase in the direction of spontaneous reaction.

(b) The condition for equilibrium is $G_{\text{N}_2} + 3G_{\text{H}_2} = 2G_{\text{NH}_3}$ where G is Gibbs free energy per mole of the gaseous species measured at their partial pressures. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent.

- (c) The catalyst will increase the rate of forward reaction.
 (d) Catalyst will not alter the rate of either of the reaction.

28. A schematic plot of $\ln K_{\text{eq}}$ versus inverse of temperature for a reaction is shown in the figure:



The reaction must be

- (a) exothermic
 (b) endothermic
 (c) one with negligible enthalpy change
 (d) highly spontaneous at ordinary temperature.

29. A solution was made by dissolving 3.75 g of a pure hydrocarbon in 95.0 g of acetone. The boiling point of pure acetone was observed to be 55.95°C and of the solution, 56.50°C . If the molal boiling point constant of acetone is $1.71^\circ\text{C kg/mol}$. The approximate molecular mass of the hydrocarbon is

- (a) 123 (b) 149
 (c) 217 (d) 227

30. In the equilibrium $\text{AB} \rightleftharpoons \text{A} + \text{B}$; if the equilibrium concentration of A is doubled, the equilibrium concentration of B would become

- (a) twice (b) half
 (c) $1/4\text{th}$ (d) $1/8\text{th}$

SOLUTIONS

1. (a) : Work done depends upon the path adopted, so it is not a state function.

2. (a) : Suppose atomic masses of A and B are x and y, respectively.

$$\text{Molar mass of } AB_2 = x + 2y$$

$$1 \text{ g } AB_2 = \frac{1}{x + 2y} \text{ mol}$$

$$\text{Molar mass of } AB_4 = x + 4y$$

$$1 \text{ g } AB_4 = \frac{1}{x + 4y} \text{ mol}$$

$$m(AB_2) = \frac{1/(x + 2y)}{20} \times 1000 = \frac{50}{x + 2y}$$

$$\Delta T_f = K_f \times m$$

$$2.3 = 5.1 \times \frac{50}{x + 2y}$$

$$\text{or } x + 2y = 110.87 \quad \dots(i)$$

Similarly, for the 2nd case

$$x + 4y = 196.15 \quad \dots(ii)$$

Solving eqs (i) and (ii), we get

$$x = 25.59; y = 42.64$$

3. (b) : 0.01 M $\text{CaCl}_2 \equiv 0.02 \text{ M } \text{Cl}^-$,

$$0.01 \text{ M } \text{NaCl} \equiv 0.01 \text{ M } \text{Cl}^-$$

$$0.05 \text{ M } \text{AgNO}_3 \equiv 0.05 \text{ M } \text{Ag}^+$$

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp}$$

$$\text{Hence, } S_2 = \frac{K_{sp}}{0.02} = 50K_{sp}, S_3 = \frac{K_{sp}}{0.01} = 100K_{sp},$$

$$S_4 = \frac{K_{sp}}{0.05} = 20K_{sp},$$

S_1 is maximum because of high dielectric constant of water.

Thus, the order is $S_1 > S_3 > S_2 > S_4$.

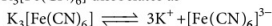
4. (a) : $\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{OH}; \Delta H = -ve$

$$\Delta_r H = \sum \Delta_f H_{(\text{products})} - \sum \Delta_f H_{(\text{reactants})}$$

$$\Delta_r H = y - x = -ve \text{ hence, } x > y.$$

$$5. (c) : i = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{cal}}} = \frac{0.062}{1.86 \times 0.01} = 3.33$$

Now, $\text{K}_3[\text{Fe}(\text{CN})_6]$ dissociates as

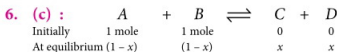


$$\begin{array}{ccc} \text{Initially} & 1 & 0 \\ \text{At equil.} & 1-\alpha & 3\alpha \end{array}$$

Total number of moles after dissociation

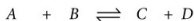
$$= 1 + 3\alpha = i$$

$$\alpha = \frac{i-1}{3} = \frac{3.33-1}{3} = 0.777 \text{ or } 77.7\% = 78\%$$



According to question : $x = 2(1-x)$,

$$\text{or, } x = \frac{2}{3}$$



$$\text{Equil. conc.: } \left(1 - \frac{2}{3}\right) \quad \left(1 - \frac{2}{3}\right) \quad \frac{2}{3} \quad \frac{2}{3}$$

Equilibrium constant,

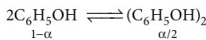
$$K = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{\frac{2}{3} \times \frac{2}{3}}{\left(1 - \frac{2}{3}\right) \left(1 - \frac{2}{3}\right)} = 4$$

7. (a) : The change given is occurring at the boiling point of the liquid, where at given pressure and temperature, the liquid-vapour system virtually remains at equilibrium and hence, $\Delta G = 0$. Also, due to absorption of heat as latent heat of vaporisation, or due to change from liquid to gaseous state, randomness has also increased i.e., $\Delta S > 0$.

$$8. (a) : M_{2(\text{obs.})} = \frac{K_f \times W_2 \times 1000}{W_1 \times \Delta T_f} = \frac{5.12 \times 2.0 \times 10^{-2} \times 1000}{1.0 \times 0.69} = 148.4$$

Calculated molecular mass of phenol = 94

$$i = \frac{M_{2(\text{cal})}}{M_{2(\text{obs})}} = \frac{94}{148.4} = 0.633$$



$$\text{Total species} = (1-\alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{1-\alpha/2}{1} \quad \text{or} \quad \frac{\alpha}{2} = 1-i$$

$$\text{or } \alpha = 2(1-i) = 2(1-0.633) = 0.734 = 73.4\%$$

9. (c) : Due to dilution on mixing equal volumes, conc. is halved in each case.

$$(a) K_{ip} = \frac{3}{2} \times 10^{-6} \times \frac{3}{2} \times 10^{-6} = 2.25 \times 10^{-12}$$

$$(b) K_{ip} = \frac{4}{2} \times 10^{-6} \times \frac{3}{2} \times 10^{-6} = 3 \times 10^{-12}$$

$$(c) K_{ip} = \frac{6}{2} \times 10^{-6} \times \frac{3}{2} \times 10^{-6} = 4.5 \times 10^{-12}$$

$$(d) K_{ip} = \frac{1}{2} \times 10^{-6} \times \frac{4}{2} \times 10^{-6} = 1 \times 10^{-12}$$

Therefore, CaSO_4 is precipitated in case (c) because here $K_{ip} > K_{sp}$.

10. (b) : For endothermic reaction, $\Delta H = +ve$

Now, $\Delta G = \Delta H - T\Delta S$

ΔG will be +ve (non-spontaneous reaction) when $\Delta H > (-T\Delta S)$ i.e., when temperature is low and ΔS is positive.

ΔG will be -ve (spontaneous reaction) when $\Delta H < (-T\Delta S)$ i.e., when temperature is high and ΔS is positive.

11. (a) : $A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$

$$i = 1 - \alpha + x\alpha + y\alpha = 1 + \alpha(x + y - 1)$$

$$\therefore \alpha = \frac{i - 1}{(x + y - 1)}$$

12. (d) : $\text{Cl}_{2(g)} + 3\text{F}_{2(g)} \rightleftharpoons 2\text{ClF}_{3(g)}$
 $\Delta H = -329 \text{ kJ mol}^{-1}$

Favourable conditions:

- As the reaction is exothermic, hence decrease in temperature will favour the forward reaction.
- Addition of reactants or removal of product will favour the forward reaction.
- Here $\Delta n = 2 - 4 = -2$ (i.e., -ve) hence decrease in volume or increase in pressure will favour the forward reaction.

13. (d) : For reaction IV, $\Delta H = -ve$ and $\Delta S = +ve$, hence $\Delta G = -ve$ at all temperatures.

14. (c) : $P_T = p_X^\circ x_X + p_Y^\circ x_Y$

where, P_T = Total pressure

p_X° = Vapour pressure of X in pure state

p_Y° = Vapour pressure of Y in pure state

x_X = Mole fraction of X = 1/4

x_Y = Mole fraction of Y = 3/4

(i) When $T = 300 \text{ K}$, $P_T = 550 \text{ mm Hg}$

$$\therefore 550 = p_X^\circ \left(\frac{1}{4}\right) + p_Y^\circ \left(\frac{3}{4}\right)$$

$$\Rightarrow p_X^\circ + 3p_Y^\circ = 2200 \quad \dots(1)$$

(ii) When at $T = 300 \text{ K}$, 1 mole of Y is added,

$$P_T = (550 + 10) \text{ mm Hg} = 560 \text{ mm Hg}$$

$$\therefore x_X = 1/5 \text{ and } x_Y = 4/5$$

$$\Rightarrow 560 = p_X^\circ \left(\frac{1}{5}\right) + p_Y^\circ \left(\frac{4}{5}\right)$$

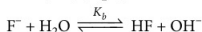
$$\text{or } p_X^\circ + 4p_Y^\circ = 2800 \quad \dots(2)$$

On solving equations (1) and (2), we get

$$p_Y^\circ = 600 \text{ mm Hg and } p_X^\circ = 400 \text{ mm Hg.}$$

15. (c) : $\text{HF} + \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{H}_3\text{O}^+ + \text{F}^-$

$$\text{or } K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$



$$\text{or } K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-][\text{H}_2\text{O}]}$$

$$\therefore K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 10^{-14}$$

Given $\text{p}K_b = 10.83$

$$\therefore K_b = 1.48 \times 10^{-11} \quad (\because \text{p}K_b = -\log K_b)$$

$$\therefore K_a = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.76 \times 10^{-4}$$

16. (c) : $\text{C}_6\text{H}_5\text{COOH}_{(s)} + \frac{15}{2} \text{O}_{2(g)} \longrightarrow 7\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$

$$\Delta n = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$$

$$= 7 - \frac{15}{2} = -\frac{1}{2}$$

$$q_p = q_v + \Delta nRT$$

$$q_p = -321.30 + \left(-\frac{1}{2}\right) \times R \times 300$$

$$q_p = -321.30 - 150R$$

17. (a) : Volume of 100 g of $\text{Al}_2(\text{SO}_4)_3 = \frac{100}{1.253} = 79.8 \text{ mL}$

Amount of $\text{Al}_2(\text{SO}_4)_3$ in 79.8 mL = 22.0 g

$$\text{Molarity} = \frac{\text{Mass of solute in gram per litre}}{\text{Molar mass of solute}}$$

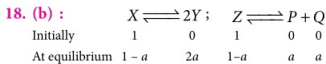
$$= \frac{22.0}{79.8} \times \frac{1000}{342} = 0.806 \text{ M}$$

$$\text{Normality} = \frac{\text{Mass of solute in gram per litre}}{\text{Equivalent weight of solute}}$$

$$= \frac{22.0}{79.8} \times \frac{1000}{56.99} = 4.84 \text{ N}$$

$$\text{Molality} = \frac{\text{Mass of solute per kg of solvent}}{\text{Molar mass of the solute}}$$

$$= \frac{22.0}{78.0} \times \frac{1000}{342} = 0.825 \text{ m}$$



$$K_{p_1} = \frac{p_Y^2}{p_X} = \frac{\left(\frac{2a}{1+a} P_1\right)^2}{\left(\frac{1-a}{1+a} P_1\right)}$$

$$K_{p_2} = \frac{p_P p_Q}{p_Z} = \frac{\left(\frac{a}{1+a} P_2\right) \left(\frac{a}{1+a} P_2\right)}{\left(\frac{1-a}{1+a} P_2\right)}$$

$$\Rightarrow K_{p_1} = \frac{4a^2 P_1}{1-a^2} \quad \dots(i)$$

$$\Rightarrow K_{p_2} = \frac{a^2 P_2}{1-a^2} \quad \dots(ii)$$

$$\text{Given } \frac{K_{p_1}}{K_{p_2}} = \frac{1}{9} \quad \dots(iii)$$

Substituting values from equations (i) and (ii) into (iii), we get

$$\frac{4a^2 P_1}{1-a^2} = \frac{1}{9} \Rightarrow \frac{4P_1}{P_2} = \frac{1}{9} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

19. (c) : Energy available for muscular work

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

∴ Energy available for muscular work from

$$120 \text{ g of glucose} = 720 \times \frac{120}{180} = 480 \text{ kJ}$$

(Molecular mass of glucose = 180)

∴ 100 kJ of energy is used for walking = 1 km

∴ 480 kJ of energy is used for walking

$$= 1 \times \frac{480}{100} = 4.8 \text{ km}$$

20. (a) : Molecular mass of solute (M_2)

$$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$M_2 = \frac{2.53 \times 2 \times 1000}{0.88 \times 90} = 63.9$$

NaCl being ionic does not dissolve in benzene.

Molecular mass of $\text{CO}(\text{NH}_2)_2 = 60$

Molecular mass of $\text{C}_6\text{H}_{12}\text{O}_6 = 180$

∴ Non-volatile solute could be urea,



21. (c) : For 1st case,

$$\text{pH} = \text{p}K_{\text{HA}} + \log \frac{[\text{Salt}]}{[\text{HA}]}$$

$$4 = -\log 10^{-5} + \log \frac{[\text{Salt}]}{0.5}$$

$[\text{Salt}] = 0.05 \text{ M} = \text{NaA}$; $\text{HA} = 0.5 \text{ M}$

For 2nd case, $6 = -\log 10^{-5} + \log \frac{[\text{Salt}]}{0.5}$

$[\text{Salt}] = 5 \text{ M} = \text{NaA}$; $\text{HA} = 0.5 \text{ M}$

In a new mixture of both buffers having equal volumes.

$$[\text{NaA}] = \frac{0.05 \text{ V} + 5 \text{ V}}{2 \text{ V}} = \frac{5.05}{2} \text{ M}$$

$$[\text{HA}] = \frac{0.5 \text{ V} + 0.5 \text{ V}}{2 \text{ V}} = 0.5 \text{ M}$$

$$\text{pH} = -\log 10^{-5} + \log \frac{5.05}{2 \times 0.5} = 5.70$$

22. (b) : As it absorbs heat,

$$\therefore q = +208 \text{ J}$$

$$w_{\text{rev}} = -2.303nRT \log \left(\frac{V_2}{V_1} \right)$$

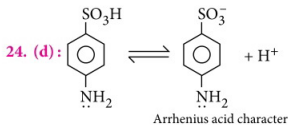
$$w_{\text{rev}} = -2.303 \times 0.04 \times 8.314 \times 310 \log \left(\frac{375}{50} \right)$$

$$\therefore w_{\text{rev}} = -207.76 \approx -208 \text{ J}$$

23. (d) : The extent of depression in freezing point varies with the number of solute particles for a fixed solvent only and it is a characteristic feature of the nature of solvent also.

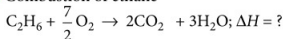
$$\Delta T_f = K_f \times m$$

For different solvents, value of K_f is also different. So, for two different solvents, the extent of depression may vary even if their molality is same.



It can also act as Lewis base since a lone pair is present on nitrogen.

- 25. (a) :** Combustion of ethane



$$\Delta H_f : -21.0 \quad 0 \quad 2 \times -94.1 \quad 3 \times -68.3$$

(kcal)

$$\begin{aligned}\Delta H^\circ_{\text{Reaction}} &= \Sigma \Delta H^\circ_{f(\text{Products})} - \Sigma \Delta H^\circ_{f(\text{Reactants})} \\ &= 2(-94.1) + 3(-68.3) - (-21.0) \\ &= -372.1 \text{ kcal}\end{aligned}$$

- 26. (b)**

27. (b): At equilibrium, at a particular temperature the concentrations of reactants and products will be same (not equal) whether the reaction is carried out in presence or absence of catalyst. A catalyst simply helps to attain the equilibrium quickly by lowering the activation energy.

- $$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$
- $$\ln \frac{6}{2} = \frac{\Delta H}{R} [1.5 \times 10^{-3} - 2 \times 10^{-3}]$$

$$\text{or, } \ln 3 = \frac{\Delta H}{R} \times (-0.5 \times 10^{-3})$$

ΔH of reaction comes out to be negative. Hence, reaction is exothermic.

- 29. (a) :** $\Delta T_b = K_b \times m$

$$(56.50 - 55.95)^{\circ}\text{C} = 1.71 \times m$$

$$m = 0.322 \text{ mol/kg}$$

1 kg of solvent contains 0.322 moles of solute, hydrocarbon. Then, 0.0950 kg of solvent contains $0.322 \times 0.0950 = 0.0306$ moles of solute.

Now, 0.0306 moles of solute = 3.75 g

$$1 \text{ mol} = \frac{3.75}{0.0306} = 122.55 \approx 123 \text{ g}$$

Molecular mass = 123

- 30. (b):** For reaction, $AB \rightleftharpoons A + B$

$$K = \frac{[A][B]}{[A][B]} \quad \dots(i)$$

$$K = \frac{[2A][B']}{[AB]} \quad \dots(\text{ii})$$

Dividing eqn. (ii) from (i), we get

$$\frac{[2A][B']}{[A][B]} = 1$$

$$\Rightarrow 2[B'] = [B]$$

$$\Rightarrow [B'] = \frac{[B]}{2}$$



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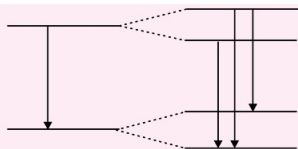
ADVANCED CHEMISTRY BLOC

(SOMMERFELD'S ROSETTE AND HIESENBERG'S PRINCIPLE)

Mukul C. Ray, Odisha

These two independent points are there in the Class-XI syllabus. As has been our objective in this bloc, we will try to analyze these two points so as to gain slightly better and more realistic ideas.

When viewed using high resolving instruments, each line of hydrogen spectrum was found to contain some finer lines. Now it was a challenge before the scientific world to come up with a theoretical solution to this observation. The principal idea was to create sublevels of energy within each principal level.

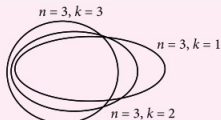


Only one line in between two energy levels (left part)
but if each level is split into more levels
there will be more lines (right part)

Now, how to break one level to sublevels? Sommerfeld suggested electronic orbit could be elliptical as well with nucleus at one of its foci. Circular orbit is a special case of ellipse. He suggested two quantum numbers; principal (n) and azimuthal quantum number (k) so that the ratio between them is

$$\frac{n}{k} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

Consider for example third shell for which $n=3$; the sublevels are



Three sublevels of energy level $n=3$. The nucleus is at the center of the circular path and that coincides with one of the foci of both the ellipses

But how energy of electron becomes different while moving in an elliptical orbit of different eccentricity and the circular orbit. There is a law called, **Kepler's law of equal area**. It says **while moving in an elliptical orbit with one of the foci of the ellipse as the center, the body sweeps equal area in equal interval of time**.



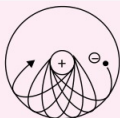
The nucleus is at point N, one of the foci.
Areas NAB and NCD are equal and covered in equal time.

This means while the body is at the perihelion point of the ellipse, it moves faster. This increase in the velocity of the body of electron at the perihelion point brings correction to its mass. Now its relativistic mass increases.

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where ' m_0 ' is the rest mass of the electron and ' m ' is the mass of the electron when it is moving with velocity ' v ' units. This change in mass brings change in energy of the electron.

There is another consequence of the fast movement at the perihelion point. **The electron tends to overshoot its orbit. It implies, unknowingly it tends to leave the orbit.** But how can it be possible? Rather the equilibrium position is disturbed and the major axis of the ellipse shifts. The perihelion point rotates with nucleus pinned at the focus of the ellipse. This path is called *rosette*.



Sommerfeld's elliptical orbit precessing about the focus of the ellipse—the path is called rosette

In fact, all theoretical calculations regarding motion of Mercury around the Sun comes close to the true observation up to 100% only when relativistic correction of mass of the planet is considered as it comes close to the Sun while revolving in its oval shaped orbit. The motion of electron as per Sommerfeld's model is similar to motion of Mercury planet around the Sun.

Uncertainty Principle

To know the position and velocity of an automobile while moving, the best idea is to crash it against another automobile which is not logical.



Now I know your position!!!

There can be no other particle smaller than an electron. So to detect position and velocity of an electron, another electron (or a photon) is crashed against it. The size of a photon of wavelength λ is at least λ and this introduces automatically an uncertainty in position by an amount λ thus $\Delta x = \lambda$. The momentum of a photon is h/λ . If it transfers its entire momentum to the electron, the momentum of an electron would become higher by an amount h/λ . So the maximum uncertainty in the determination of momentum becomes h/λ thus $\Delta p = h/\lambda$. And $\Delta x \Delta p = h$. By a careful thorough experiment Heisenberg confirmed that $\Delta x \Delta p \geq h/4\pi$.

There is no restrictions on the values of Δx nor even on Δp rather the restriction is on multiplication of Δx and Δp . If you know exactly the position of an electron then Δx becomes zero but now Δp becomes infinite or nothing is known about the momentum of electron. These are not random or systematic errors. Even in an ideal world where these errors are absent, the uncertainty of momentum and position of electron would survive. This is the law of nature. It states that **the position and the momentum of the electron cannot be determined simultaneously with accuracy.** In short, limitations are set on real world behaviour by Heisenberg's principle, which among other things include the maximum resolving power of microscope, the ultimate size of a computer chip etc.

There is another form of uncertainty principle $\Delta E \Delta t \geq h/4\pi$, where Δt is the time taken to measure the energy of a state and ΔE is the uncertainty in the measured value of energy. Suppose an electron spends one nano second in the excited energy level of the atom; the minimum uncertainty in the value of energy of the excited level is

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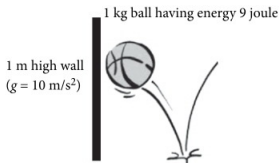
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$$\Delta E \geq \frac{6.6 \times 10^{-34}}{4\pi \times 1.0 \times 10^{-9}} = 5.3 \times 10^{-26} \text{ joule}$$

Longer the time taken to measure the energy, the more accurate will be the prediction of energy. There is an interesting application of this principle. Say a ball of 1 kg mass having energy 9 joules is trying to cross a 1 m high wall. To cross over the wall and to go to the other side the ball would have to spend 10 joules of energy ($mgh = 1 \times 10 \times 1 = 10$ joules). As per classical physics this is not possible. Doing so it would violate the law of conservation of energy by an amount 1.0 joule.



A 1 kg ball trying to cross a 1 m high wall that requires energy 10 joules

According to Heisenberg's principle, the ball can cross the wall provided the time it takes to complete this task is

$$\Delta t \approx \frac{h}{4\pi \times \Delta E} = \frac{6.6 \times 10^{-34}}{4\pi \times 1.0} = 5.3 \times 10^{-35} \text{ s}$$

This is too small for a macroscopic object and the 1 kg ball has to travel at a speed many times faster than that of light to cross the wall. The conclusion is that the ball cannot make it over the wall even though theoretically it could.

Now consider an electron having energy 1.0 eV. It has to cross a barrier having energy 2.0 eV. This would violate the conservation of energy principle by 1.0 eV. The time interval over which this has to happen is

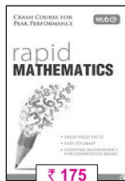
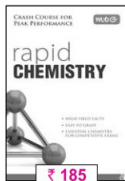
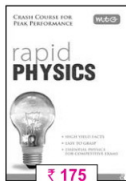
$$\Delta t \approx \frac{h}{4\pi \times \Delta E} = \frac{6.6 \times 10^{-34}}{4\pi \times 1.0 \times 1.6 \times 10^{-19}} = 3.3 \times 10^{-16} \text{ s}$$

A fast electron can make it and it really does. Thus, the conclusion is that **the law of conservation of energy can be violated provided the time that it takes to happen is not too long.**

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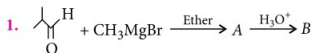
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The IUPAC name of 'B' is

- 3-methylbutan-2-ol
- 2-methylbutan-3-ol
- 2-methylbutan-2-ol
- pentan-2-ol.

2. For Freundlich isotherm a graph of $\log \frac{x}{m}$ is plotted against $\log P$. The slope of the line and its y-axis intercept, respectively corresponds to

- $\frac{1}{n}, k$
- $\log \frac{1}{n}, k$
- $\frac{1}{n}, \log k$
- $\log \frac{1}{n}, \log k$

3. A plot of $\frac{1}{T}$ vs k for a reaction gives the slope -1×10^4 K. The energy of activation for the reaction is

(Given : $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

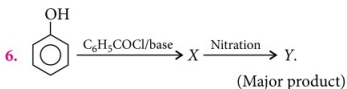
- 8314 J mol^{-1}
- 1.202 kJ mol^{-1}
- 12.02 J mol^{-1}
- 83.14 kJ mol^{-1}

4. The IUPAC name of the complex ion formed when gold dissolves in aqua regia is

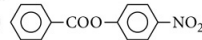
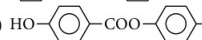
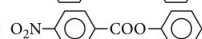
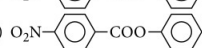
- tetrachloridoaurate (III)
- tetrachloridoaurate (I)
- tetrachloridoaurate (II)
- dichloridoaurate (III).

5. The correct sequence of reactions to be performed to convert benzene into *m*-bromoaniline is

- nitration, reduction, bromination
- bromination, nitration, reduction
- nitration, bromination, reduction
- reduction, nitration, bromination.



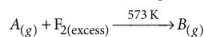
Y is

- 
- 
- 
- 

7. $\text{A}_{(g)} \xrightarrow{\Delta} \text{P}_{(g)} + \text{Q}_{(g)} + \text{R}_{(g)}$, follows first order kinetics with a half-life of 69.3 s at 500°C . Starting from the gas 'A' enclosed in a container at 500°C and at a pressure of 0.4 atm, the total pressure of the system after 230 s will be

- 1.15 atm
- 1.32 atm
- 1.22 atm
- 1.12 atm

8. $\text{MnO}_2 + \text{HCl} \xrightarrow{\Delta} \text{A}_{(g)}$



The gases A, B, C and D are respectively

- $\text{Cl}_2, \text{ClF}, \text{UF}_6, \text{ClF}_3$
- $\text{Cl}_2, \text{ClF}_3, \text{UF}_6, \text{ClF}$
- $\text{O}_2, \text{OF}_2, \text{U}_2\text{O}_3, \text{O}_2\text{F}_2$
- $\text{O}_2, \text{O}_2\text{F}_2, \text{U}_2\text{O}_3, \text{OF}_2$

9. Acetophenone cannot be prepared easily starting from

- $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$
- $\text{C}_6\text{H}_5\text{CH}_3$
- $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$
- C_6H_6

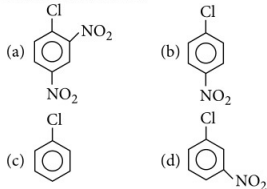
10. One mole of ammonia was completely absorbed in one litre solution each of (1) 1 M HCl, (2) 1 M CH_3COOH and (3) 1 M H_2SO_4 at 298 K. The decreasing order for the pH of the resulting solutions is

(Given : $K_b(\text{NH}_3) = 4.74$)

- (a) $2 > 3 > 1$ (b) $1 > 2 > 3$
(c) $2 > 1 > 3$ (d) $3 > 2 > 1$
11. 5.5 mg of nitrogen gas dissolves in 180 g of water at 273 K and one atm pressure due to nitrogen gas. The mole fraction of nitrogen in 180 g of water at 5 atm nitrogen pressure is approximately
- (a) 1×10^{-6} (b) 1×10^{-5}
(c) 1×10^{-3} (d) 1×10^{-4}
12. 50 cm^3 of 0.04 M $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium oxidizes a sample of H_2S gas to sulphur. Volume of 0.03 M KMnO_4 required to oxidize the same amount of H_2S gas to sulphur, in acidic medium is

- (a) 60 cm^3 (b) 80 cm^3
(c) 90 cm^3 (d) 120 cm^3

13. The compound that reacts the fastest with sodium methoxide is



14. The pair of compounds having identical shapes for their molecules is

- (a) CH_4 , SF_4 (b) BCl_2 , ClF_3
(c) XeF_2 , ZnCl_2 (d) SO_2 , CO_2

15. Conductivity of a saturated solution of a sparingly soluble salt AB at 298 K is $1.85 \times 10^{-5} \text{ S m}^{-1}$. Solubility product of the salt AB at 298 K is

- (Given : $\Lambda_m^\circ(\text{AB}) = 140 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$)
- (a) 5.7×10^{-12} (b) 1.32×10^{-12}
(c) 7.5×10^{-12} (d) 1.74×10^{-12}

16. An incorrect statement with respect to $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms for alkyl halide is
- (a) a strong nucleophile in an aprotic solvent increases the rate or favours $\text{S}_{\text{N}}2$ reaction
(b) competing reaction for an $\text{S}_{\text{N}}2$ reaction is rearrangement
(c) $\text{S}_{\text{N}}1$ reactions can be catalysed by some Lewis acids
(d) a weak nucleophile and a protic solvent increases the rate or favours $\text{S}_{\text{N}}1$ reaction.

17. Butylated hydroxy toluene as a food additive acts as
- (a) antioxidant (b) flavouring agent
(c) colouring agent (d) emulsifier.

18. Terylene is NOT a
- (a) copolymer
(b) polyester fibre
(c) chain growth polymer
(d) step growth polymer.

19. The correct statement is
- (a) cyclohexadiene and cyclohexene cannot be isolated with ease during controlled hydrogenation of benzene
(b) one mole each of benzene and hydrogen when reacted gives 1/3 mole of cyclohexane and 2/3 mole unreacted hydrogen
(c) hydrogenation of benzene to cyclohexane is an endothermic process
(d) it is easier to hydrogenate benzene when compared to cyclohexene.

20. Among the elements from atomic number 1 to 36, the number of elements which have an unpaired electron in their s-subshell is
- (a) 4 (b) 7
(c) 6 (d) 9

21. The statement that is NOT correct is
- (a) compressibility factor measures the deviation of real gas from ideal behaviour
(b) van der Waals constant 'a' measures extent of intermolecular attractive forces for real gases
(c) critical temperature is the lowest temperature at which liquefaction of a gas first occurs
(d) Boyle point depends on the nature of real gas.

22. The correct arrangement for the ions in the increasing order of their radii is
 (a) Na^+ , Cl^- , Ca^{2+} (b) Ca^{2+} , K^+ , S^{2-}
 (c) Na^+ , Al^{3+} , Be^{2+} (d) Cl^- , F^- , S^{2-}
23. The correct arrangement of the species in the decreasing order of the bond length between carbon and oxygen in them is
 (a) CO , CO_2 , HCO_3^- , CO_3^{2-}
 (b) CO_2 , HCO_3^- , CO , CO_3^{2-}
 (c) CO_3^{2-} , HCO_3^- , CO_2 , CO
 (d) CO , CO_3^{2-} , CO_2 , HCO_3^-
24. The species that is not hydrolysed in water is
 (a) P_4O_{10} (b) BaO_2
 (c) Mg_3N_2 (d) CaC_2
25. For the properties mentioned, the correct trend for the different species is in
 (a) strength as Lewis acid – $\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3$
 (b) inert pair effect – $\text{Al} > \text{Ga} > \text{In}$
 (c) oxidising property – $\text{Al}^{3+} > \text{In}^{3+} > \text{Tl}^{3+}$
 (d) first ionization enthalpy – $\text{B} > \text{Al} > \text{Tl}$
26. A correct statement is
 (a) $[\text{Co}(\text{NH}_3)_6]^{2+}$ is paramagnetic
 (b) $[\text{MnBr}_4]^{2-}$ is tetrahedral
 (c) $[\text{CoBr}_2(\text{en})_2]^-$ exhibits linkage isomerism
 (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an inner orbital complex.
27. Iodoform reaction is answered by all, except
 (a) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{COOH}$
 (b) CH_3CHO
 (c) $\text{CH}_3-\text{CH}_2-\text{OH}$
 (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$
28. A crystalline solid XY_3 has *ccp* arrangement for its element Y. X occupies
 (a) 66% of tetrahedral voids
 (b) 33% of tetrahedral voids
 (c) 66% of octahedral voids
 (d) 33% of octahedral voids.
29. $\text{C}_6\text{H}_5\text{COOH} \xrightarrow[2. \Delta]{1. \text{NH}_3} \text{P} \xrightarrow{\text{NaOBr}} \text{Q} \xrightarrow[2. \text{heat to } 460 \text{ K}]{1. \text{Conc. H}_2\text{SO}_4} \text{R}'$
 'R' is
 (a) *o*-bromosulphanilic acid
 (b) sulphanilamide

- (c) sulphanilic acid
 (d) *p*-bromosulphanilamide.

30. The statement that is NOT correct is
 (a) aldose or ketose sugars in alkaline medium do not isomerise
 (b) carbohydrates are optically active
 (c) penta acetate of glucose does not react with hydroxylamine
 (d) lactose has glycosidic linkage between C_4 of glucose and C_1 of galactose unit.
31. Match the reactant in column-I with the reaction in column-II.

Column-I		Column-II	
(i)	Acetic acid	(A)	Stephen
(ii)	Sodium phenate	(B)	Friedel-Crafts
(iii)	Methyl cyanide	(C)	HVZ
(iv)	Toluene	(D)	Kolbe's

- (a) i-C, ii-A, iii-D, iv-B
 (b) i-D, ii-B, iii-C, iv-A
 (c) i-B, ii-C, iii-A, iv-D
 (d) i-C, ii-D, iii-A, iv-B
32. The statement that is NOT correct is
 (a) hypophosphorous acid reduces silver nitrate to silver
 (b) in solid state PCl_5 exists as $[\text{PCl}_4]^+[\text{PCl}_6]^-$
 (c) pure phosphine is non-inflammable
 (d) phosphorous acid on heating disproportionates to give metaphosphoric acid and phosphine.
33. In which one of the pairs of ion given, there is an ion that forms a co-ordination compound with both aqueous sodium hydroxide and ammonia and an other ion that forms a co-ordination compound only with aqueous sodium hydroxide?
 (a) Pb^{2+} , Cu^{2+} (b) Zn^{2+} , Al^{3+}
 (c) Cu^{2+} , Zn^{2+} (d) Al^{3+} , Cu^{2+}
34. A crystalline solid X reacts with dil. HCl to liberate a gas Y. Y decolourises acidified KMnO_4 . When a gas Z is slowly passed into an aqueous solution of Y, colloidal sulphur is obtained. X and Z could be, respectively
 (a) Na_2S , SO_3 (b) Na_2SO_4 , H_2S
 (c) Na_2SO_3 , H_2S (d) Na_2SO_4 , SO_2

35. An aromatic compound A (C_7H_9N) on reacting with $NaNO_2/HCl$ at $0^\circ C$ forms benzyl alcohol and nitrogen gas. The number of isomers possible for the compound A is
(a) 5 (b) 7
(c) 3 (d) 6
36. The statement that is NOT correct is
(a) a furnace lined with Haematite is used to convert cast iron to wrought iron.
(b) collectors enhance the wettability of mineral particles during froth flotation.
(c) in vapour phase refining, metal should form a volatile compound.
(d) copper from its low grade ores is extracted by hydrometallurgy.
37. A solution of 1.25 g of P in 50 g of water lowers freezing point by $0.3^\circ C$. Molar mass of P is 94. $K_{f(water)} = 1.86 \text{ K kg mol}^{-1}$. The degree of association of P in water is
(a) 80% (b) 60%
(c) 65% (d) 75%
38. Volume occupied by single CsCl ion pair in a crystal is $7.014 \times 10^{-23} \text{ cm}^3$. The smallest Cs - Cs internuclear distance is equal to length of the side of the cube corresponding to volume of one CsCl ion pair. The smallest Cs to Cs internuclear distance is nearly
(a) 4.4 Å (b) 4.3 Å
(c) 4 Å (d) 4.5 Å
39. For $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$, $E^\circ = 1.33 \text{ V}$ At $[Cr_2O_7^{2-}] = 4.5 \text{ millimole}$, $[Cr^{3+}] = 15 \text{ millimole}$, E is 1.067 V. The pH of the solution is nearly equal to
(a) 2 (b) 3
(c) 5 (d) 4
40. 1.78 g of an optically active L-amino acid (A) is treated with $NaNO_2/HCl$ at $0^\circ C$. 448 cm^3 of nitrogen gas at STP is evolved. A sample of protein has 0.25% of this amino acid by mass. The molar mass of the protein is
(a) $36,500 \text{ g mol}^{-1}$ (b) $34,500 \text{ g mol}^{-1}$
(c) $35,400 \text{ g mol}^{-1}$ (d) $35,600 \text{ g mol}^{-1}$
41. 10 g of a mixture of BaO and CaO requires 100 cm^3 of 2.5 M HCl to react completely. The percentage of calcium oxide in the mixture is approximately
(Given : molar mass of BaO = 153)
- (a) 52.6 (b) 55.1
(c) 44.9 (d) 47.4
42. The ratio of heats liberated at 298 K from the combustion of one kg of coke and by burning water gas obtained from kg of coke is (Assume coke to be 100% carbon)
(Given : enthalpies of combustion of CO_2 , CO and H_2 as 393.5 kJ, 285 kJ, 285 kJ respectively all at 298 K).
(a) 0.79 : 1 (b) 0.69 : 1
(c) 0.86 : 1 (d) 0.96 : 1
43. Impure copper containing Fe, Au, Ag as impurities is electrolytically refined. A current of 140 A for 482.5 s decreased the mass of the anode by 22.26 g and increased the mass of cathode by 22.011 g. Percentage of iron in impure copper is
(Given : molar mass Fe = 55.5 g mol^{-1} , molar mass Cu = 63.54 g mol^{-1})
(a) 0.95 (b) 0.85
(c) 0.97 (d) 0.90
44. 25 cm^3 of oxalic acid completely neutralised 0.064 g of sodium hydroxide. Molarity of the oxalic acid solution is
(a) 0.064 (b) 0.045
(c) 0.015 (d) 0.032
45. The statement that is NOT correct is
(a) angular quantum number signifies the shape of the orbital.
(b) energies of stationary states in hydrogen like atoms is inversely proportional to the square of the principal quantum number.
(c) total number of nodes for 3s orbital is three.
(d) the radius of the first orbit of He^+ is half that of the first orbit of hydrogen atom.
46. For the equilibrium :
 $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$; $K_p = 1.64 \text{ atm}$ at 1000 K
50 g of $CaCO_3$ in a 10 litre closed vessel is heated to 1000 K. Percentage of $CaCO_3$ that remains unreacted at equilibrium is
(Given : $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)
(a) 40 (b) 50
(c) 60 (d) 20

47. Conversion of oxygen into ozone is non-spontaneous at

- (a) all temperatures (b) high temperature
(c) room temperature (d) low temperature.

48. Density of carbon monoxide is maximum at

- (a) 2 atm and 600 K (b) 0.5 atm and 273 K
(c) 6 atm and 1092 K (d) 4 atm and 500 K.

49. The acid strength of active methylene group in


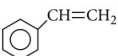
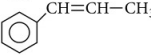
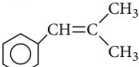
- (i) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$
(ii) $\text{CH}_3\text{COCH}_2\text{COCH}_3$
(iii) $\text{C}_2\text{H}_5\text{OOCCH}_2\text{COOC}_2\text{H}_5$ decreases as
(a) i > iii > ii (b) i > ii > iii
(c) ii > i > iii (d) iii > i > ii

50. A metallic oxide reacts with water to form its hydroxide, hydrogen peroxide and also liberates oxygen. The metallic oxide could be

- (a) CaO (b) KO_2
(c) Li_2O (d) Na_2O_2

51. $X \xrightarrow[\text{(Reductive)}]{\text{Ozonolysis}} Y + Z$

Y can be obtained by Etard's reaction. Z undergoes disproportionation reaction with concentrated alkali. X could be

- (a) 
(b) 
(c) 
(d) 

52. Gold sol is not

- (a) a macromolecular colloid
(b) a lyophobic colloid
(c) a multimolecular colloid
(d) negatively charged colloid.

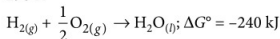
53. Carbocation as an intermediate is likely to be formed in the reaction :

- (a) Propene + $\text{Cl}_2 \xrightarrow{h\nu}$ 2-chloropropane
(b) Acetone + $\text{HCN} \xrightarrow{-\text{OH}}$ acetonecyanohydrin
(c) Ethyl bromide + Aq. KOH $\xrightarrow{\Delta}$ ethyl alcohol
(d) Hexane $\xrightarrow{\text{Anhy. AlCl}_3/\text{HCl}}$ 2-methylpentane

54. For an ideal binary liquid mixture

- (a) $\Delta S_{(\text{mix})} = 0$; $\Delta G_{(\text{mix})} = 0$
(b) $\Delta H_{(\text{mix})} = 0$; $\Delta S_{(\text{mix})} < 0$
(c) $\Delta V_{(\text{mix})} = 0$; $\Delta G_{(\text{mix})} > 0$
(d) $\Delta S_{(\text{mix})} > 0$; $\Delta G_{(\text{mix})} < 0$

55. For hydrogen – oxygen fuel cell at one atm and 298 K



E° for the cell is approximately,

- (Given : $F = 96,500 \text{ C}$)
(a) 2.48 V (b) 1.24 V
(c) 2.5 V (d) 1.26 V

56. Which one of these is not known?

- (a) CuCl_2 (b) CuI_2
(c) CuF_2 (d) CuBr_2

57. The correct statement is

- (a) the earlier members of lanthanoid series resemble calcium in their chemical properties.
(b) the extent of actinoid contraction is almost the same as lanthanoid contraction.
(c) in general, lanthanoids and actinoids do not show variable oxidation states.
(d) Ce^{4+} in aqueous solution is not known.

58. $P \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{CH}_3\text{MgBr}} R \xrightarrow[2. \Delta]{1. \text{dil. NaOH}}$ 4-methylpent-3-en-2-one

P is

- (a) propanone (b) ethanamine
(c) ethanenitrile (d) ethanal.

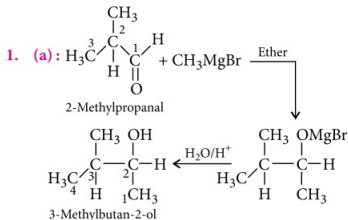
59. When $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$ reacts with one mole of HI, one of the products formed is

- (a) ethane (b) ethanol
(c) iodoethene (d) ethanal.

60. 0.44 g of a monohydric alcohol when added to methylmagnesium iodide in ether liberates at S.T.P., 112 cm^3 of methane. With PCC the same alcohol forms a carbonyl compound that answers silver mirror test. The monohydric alcohol is

- (a) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$
 (b) $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
 (d) $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{OH}$

SOLUTIONS



2. (c): Mathematically, Freundlich adsorption isotherm can be written as,

$$\underbrace{\log \frac{x}{m}}_y = \underbrace{\log k + \frac{1}{n} \log P}_c \quad \underbrace{\log P}_x$$

intercept slope

3. (None): Correction in the question : It should be $\ln k$ vs $1/T$

Plot of $\ln k$ vs $1/T$ gives

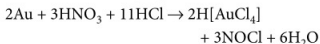
$$\text{Slope} = -\frac{E_a}{R}$$

$$\Rightarrow -1 \times 10^4 = -\frac{E_a}{8.314}$$

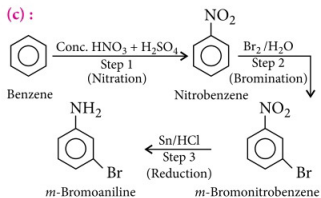
$$E_a = 8.314 \times 10^4 \text{ J mol}^{-1} = 83.14 \times 10^3 \text{ J mol}^{-1}$$

or $E_a = 83.14 \text{ kJ mol}^{-1}$

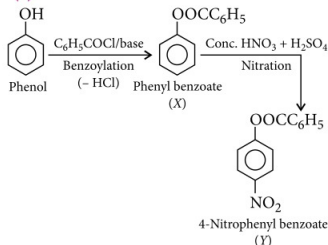
4. (a): When gold dissolves in aqua regia, it gives tetrachloridoaurate(III) anion.



5. (c):



6. (a):



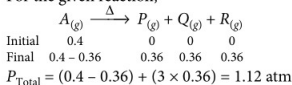
7. (d): $t_{1/2} = 69.3 \text{ s}$, $t = 230 \text{ s}$, $a = 0.4 \text{ atm}$
 For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01 \text{ s}^{-1}$$

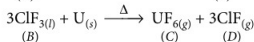
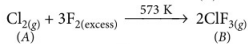
$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{230} \log \frac{0.4}{0.4-x}$$

$$\Rightarrow x = 0.36$$

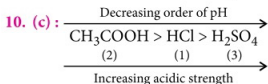
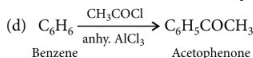
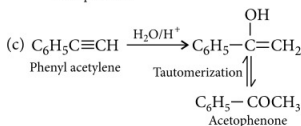
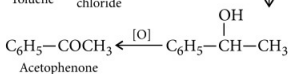
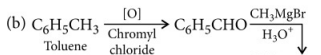
For the given reaction,



8. (b): $\text{MnO}_2 + 4\text{HCl} \xrightarrow{\Delta} \text{Cl}_{2(g)} + \text{MnCl}_2 + 2\text{H}_2\text{O}$



9. (b): (a) $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3 \xrightarrow{[\text{O}]} \text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$
 Methyl phenyl carbinol Acetophenone



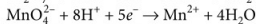
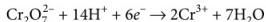
11. (c): Solubility of a gas \propto mole fraction

$$n_{\text{N}_2} = \frac{5.5 \times 10^{-3}}{28} = 1.96 \times 10^{-4} \text{ at 1 atm}$$

Now, $p \propto$ mole fraction, then at 5 atm, the mole fraction will increase 5 times.

$$\text{Hence, } 5 \times 1.96 \times 10^{-4} = 9.8 \times 10^{-4} \\ \approx 10 \times 10^{-4} = 1.0 \times 10^{-3}$$

12. (b): $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 both are good oxidizing agents in acidic medium. The reaction is as follows:



$$\begin{aligned} \text{Normality of } \text{Cr}_2\text{O}_7^{2-} &= \text{Molarity} \times \text{no. of electrons involved} \\ &= 0.04 \times 6 = 0.24 \text{ N} \end{aligned}$$

$$\begin{aligned} \text{Normality of } \text{MnO}_4^{2-} &= \text{Molarity} \times \text{no. of electrons involved} \\ &= 0.03 \times 5 = 0.15 \text{ N} \end{aligned}$$

$$\text{N}_1\text{V}_1 = \text{N}_2\text{V}_2 \Rightarrow 0.24 \times 50 = 0.15 \times \text{V}_2$$

($\text{K}_2\text{Cr}_2\text{O}_7$) (KMnO_4)

$$\text{V}_2 = \frac{0.24 \times 50}{0.15} = 80 \text{ cm}^3$$

13. (a): Electron withdrawing groups ($-\text{NO}_2$) increase the reactivity of the aryl halide ($-\text{ArCl}$). Hence, 2,4-dinitrochlorobenzene reacts fastest.

14. (c): XeF_2 is linear in shape with 2 bond pairs and 3 lone pairs of electrons. ZnCl_2 is also linear in shape with 2 bond pairs of electrons.

15. (d): Using the relationship between solubility of sparingly soluble salt and Λ_m° ,

$$\kappa = 1.85 \times 10^{-5} \text{ S m}^{-1} = 1.85 \times 10^{-7} \text{ S cm}^{-1}$$

$$\Lambda_m^\circ = 140 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} = 140 \text{ S cm}^2 \text{ mol}^{-1}$$

$$s = \frac{\kappa \times 1000}{\Lambda_m^\circ} = \frac{1.85 \times 10^{-7} \times 1000}{140} = 1.32 \times 10^{-6}$$

$$K_{sp} = (s)^2 \quad [\text{For AB type of salt}]$$

$$= (1.32 \times 10^{-6})^2 = 1.74 \times 10^{-12}$$

16. (b) 17. (a) 18. (c)

19. (a): During the hydrogenation of benzene, only cyclohexane can be isolated.

20. (c): ${}_1\text{H} = 1s^1$; ${}_3\text{Li} = 2s^1$; ${}_{11}\text{Na} = 3s^1$; ${}_{19}\text{K} = [\text{Ar}] 4s^1$
 ${}_{24}\text{Cr} = [\text{Ar}] 3d^5 4s^1$; ${}_{29}\text{Cu} = [\text{Ar}] 3d^{10} 4s^1$

21. (c): Critical temperature is the temperature above which a gas cannot be liquefied irrespective of the pressure applied.

22. (b): The species Ca^{2+} , K^+ and S^{2-} are isoelectronic. For isoelectronic ions, the radius decreases as the nuclear charge increases. Hence, the increasing order of their radii is $\text{Ca}^{2+} < \text{K}^+ < \text{S}^{2-}$

23. (c): Bond order $\propto \frac{1}{\text{Bond length}}$

$$\text{Bond order} = \frac{\text{Bond order of each C—O bond}}{\text{Total no. of resonating structures}}$$

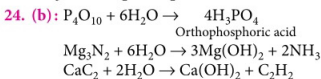
$$(a) \text{CO} \rightarrow \text{C}\equiv\text{O} \Rightarrow \frac{2+1}{1} = 3.0$$

$$(b) \text{CO}_2 \rightarrow \text{O}=\text{C}=\text{O} \Rightarrow \frac{2+2}{2} = 2.0$$

$$(c) \text{HCO}_2^- \rightarrow \text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \Rightarrow \frac{2+1}{2} = 1.5$$

$$(d) \text{CO}_3^{2-} \rightarrow \left[\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \right]^{2-} \Rightarrow \frac{1+1+2}{3} = 1.33$$

Hence, the decreasing order of bond length is $\text{CO}_3^{2-} > \text{HCO}_2^- > \text{CO}_2 > \text{CO}$.



25. (a): Lewis acid strength decreases down the group.

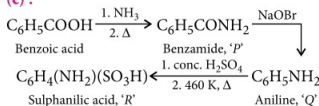
26. (a,b): (a) $[\text{Co}(\text{NH}_3)_6]^{2+}$; $_{27}\text{Co}^{2+}$: $[\text{Ar}] 3d^7 4s^0$
 $n = 3$ (where $n =$ no. of unpaired electrons)
 Hence, complex is paramagnetic in nature.
 (b) $[\text{MnBr}_4]^{2-}$: sp^3 -hybridisation (Tetrahedral)
 (c) $[\text{CoBr}_2(\text{en})_2]^-$ exhibits geometrical isomerism.
 (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$: $sp^3 d^2$ -hybridisation
 (outer orbital complex)
 Both statements (a) and (b) are correct.

27. (d)

28. (d): As ratio of X and Y is 1 : 3, X will occupy $\frac{1}{3}$ rd of octahedral voids.

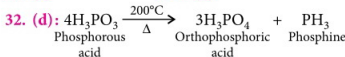
$$\therefore \% \text{ of octahedral voids occupied by } X = \frac{1}{3} \times 100 = 33.3\%$$

29. (c):

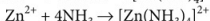
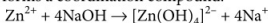


30. (a)

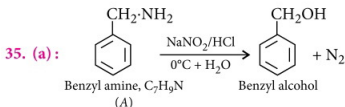
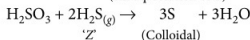
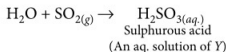
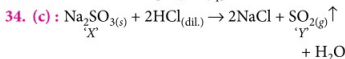
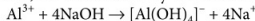
31. (d)



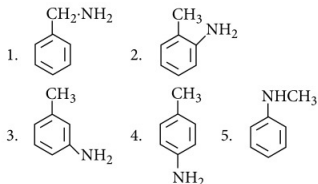
33. (b): Zn^{2+} ion reacts with aq. NaOH and NH_3 and forms a coordination compound.



But, Al^{3+} ion reacts only with NaOH .



The possible isomers of benzyl amine are :



36. (b): Collectors enhance the non-wettability of mineral particles.

37. (a): Given : $K_f = 1.86 \text{ K kg mol}^{-1}$, $w = 1.25 \text{ g}$,
 $W = 50 \text{ g}$, $\Delta T = 0.3^\circ\text{C}$, $M = ?$
 As P undergoes association,
 $2P \rightleftharpoons (P)_2$; $n = 2$

$$M = \frac{1000 \times K_f \times w}{W \times \Delta T} = \frac{1000 \times 1.86 \times 1.25}{50 \times 0.3} = 155$$

$$\text{Now, } i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{155} = 0.606$$

Then, the degree of association of P is

$$\alpha = \frac{1-i}{1-\frac{1}{n}} = \frac{1-0.606}{1-\frac{1}{2}} = 0.788 \text{ or } 78.8\% \sim 80\%$$

38. (c): Volume of $\text{CsCl} = a^3$
 $7.014 \times 10^{-23} \text{ cm}^3 = a^3$ ($a =$ edge length)
 $a = \sqrt[3]{7.014 \times 10^{-23}} = 4.12 \times 10^{-8} \text{ cm} = 4.12 \text{ \AA}$

39. (a): For the given reaction,
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$1.067 = 1.33 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2 [\text{H}_2\text{O}]^7}{[\text{Cr}_2\text{O}_7^{2-}] [\text{H}^+]^{14}}$$

$$1.067 = 1.33 - 9.85 \times 10^{-3} \log \frac{[15 \times 10^{-3}]^2 [1]^7}{[4.5 \times 10^{-3}] [\text{H}^+]^{14}}$$

$$\frac{-0.263}{-9.85 \times 10^{-3}} = 2 \log [15 \times 10^{-3}] - \log [4.5 \times 10^{-3}] - 14 \log [\text{H}^+]$$

$$26.7 = 2 \times -1.82 + 2.34 + 14 \text{ pH}$$

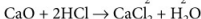
$$\Rightarrow \text{pH} = \frac{28}{14} = 2$$

40. (d): L-amino acid $\xrightarrow[0^\circ\text{C}]{\text{NaNO}_2 + \text{HCl}} \text{N}_2 \uparrow$

1 mole of L-amino acid \rightarrow 1 mole of N_2
 $= 22400 \text{ cm}^3$ of N_2 at STP
 448 cm^3 of $N_2 \equiv 1.78 \text{ g}$ of L-amino acid
 $22,400 \text{ cm}^3$ of $N_2 \equiv x \text{ g}$ of L-amino acid
 $x = \frac{1.78 \times 22,400}{448} = 89 \text{ g}$ of L-amino acid

Sample of protein has 0.25% amino acid.

Amino acid	Protein
0.25	100
89	y
$y = \frac{89 \times 100}{0.25} = 35,600 \text{ g/mol}$	



Reactions show that 2 moles of mix. of BaO and CaO requires 4 moles of HCl to react completely.

Hence, no. of moles of HCl = $\frac{2.5 \times 100}{1000} = 0.25$ moles

Now,	HCl	BaO + CaO
Initial	4 moles	2 moles
Final	0.25 moles	?

No. of moles of mixture of BaO and CaO
 $= \frac{0.25 \times 2}{4} = 0.125$ moles

Let the mass of CaO be $x \text{ g}$ and BaO is $(10 - x) \text{ g}$

Then,
 $\frac{x}{56} + \frac{10 - x}{153} = 0.125$ [Mol. mass of CaO = 56, BaO = 153]

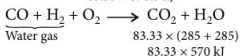
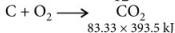
$153x + 56(10 - x) = 0.125 \times 56 \times 153$

$97x = 511 \Rightarrow x = 5.268$

$\therefore \text{ \% of CaO} = \frac{5.268}{10} \times 100 = 52.68\%$

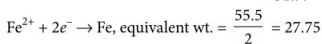
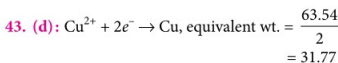
42. (b): Given information, the enthalpy of combustion of CO_2 is wrong, it should be enthalpy of combustion of C.

1 kg of coke = $\frac{1000}{12} = 83.33$ moles



Now, the ratio of

coke	:	water gas
83.33×393.5	:	83.33×570
$\Rightarrow 393.5$:	570
$\Rightarrow 0.69$:	1



Mass increased at cathode is due to deposition of Cu.

Hence, no. of gram equivalents of Cu deposited
 $= \frac{22.011}{31.77} = 0.6928$

Now, using Faraday's first law,

$Q = it = 140 \text{ A} \times 482.5 \text{ s} = 67550 \text{ C}$

$96,500 \text{ C} \rightarrow 31.77 \text{ g Cu}$

$67550 \text{ C} \rightarrow ?$

$\frac{31.77}{96,500} \times \frac{67550}{1} = 22.239 \text{ g of pure Cu deposited}$

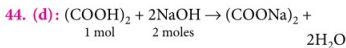
But, according to the question, the mass of cathode only increases = 22.011 g

Hence, $22.239 - 22.011 = 0.228 \text{ g}$

Now, $31.77 \text{ g Cu} \equiv 0.228 \text{ g deposited}$

$27.75 \text{ g Fe} \equiv \frac{0.228}{31.77} \times 27.75 = 0.199 \text{ g Fe deposited}$

% of Fe = $\frac{\text{Mass of Fe}}{\text{Mass of impurities (at anode)}} \times 100$
 $= \frac{0.199}{22.26} \times 100 = 0.894 \approx 0.90 \%$



Mol. mass of NaOH = 40 g mol^{-1}

No. of g moles in 0.064 g of NaOH

$= \frac{0.064}{40} = 0.0016$

No. of moles of oxalic acid = $\frac{0.0016}{2} = 8 \times 10^{-4}$

Volume of solution (in L) = $\frac{25}{1000}$

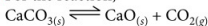
Hence, molarity = $\frac{\text{No. of moles of solute}}{\text{Volume of solution (in L)}}$
 $= 8 \times 10^{-4} \times \frac{1000}{25} = 0.032 \text{ M}$

45. (c): No. of nodes for any orbital = $n - l - 1$

For 3s-orbital, $n = 3$ and $l = 0$

Hence, no. of nodes for 3s-orbital = $3 - 1 = 2$

46. (c) : For the reaction,



$$K_c = [\text{CO}_2] \text{ or } K_p = p_{\text{CO}_2}$$

$$\text{No. of moles of CaCO}_{3(s)} = \frac{50}{100} = 0.5$$

$$PV = nRT$$

$$1.64 \times 10 = n \times 0.082 \times 1000$$

$$\text{No. of moles of CO}_2, n = 0.2$$

$$\text{No. of moles of unreacted CaCO}_3 = 0.5 - 0.2 = 0.3$$

$$\% \text{ of unreacted CaCO}_3 = \frac{0.3}{0.5} \times 100 = 60\%$$

47. (a) : $3\text{O}_{2(g)} \rightleftharpoons 2\text{O}_{3(g)}$; $\Delta H = +ve$; $\Delta S = -ve$
Equation, $\Delta G = \Delta H - T\Delta S = +ve - (-ve)$
 $\Delta G = +ve$; Non-spontaneous at all temperatures.

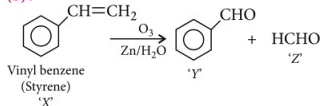
48. (d) : $d = \frac{PM}{RT} \Rightarrow d \propto \frac{P}{T}$

By using this relation, density is maximum at 4 atm and 500 K.

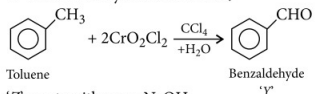
49. (c) : In active methylene compound (ii), methylene ($-\text{CH}_2-$) group exists in between two strong EWGs i.e. ($\text{CH}_3\text{CO}-$), which increases the acidity. Esters (iii) are less acidic than ketones (i) because the enolate ion produced from an ester is less stable than that produced from a ketone.

50. (b) : $2\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2 \uparrow$
Potassium superoxide

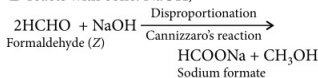
51. (b) :



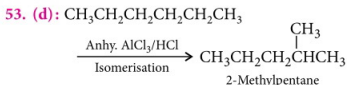
'Y' is obtained by Etard's reaction,



'Z' reacts with conc. NaOH,



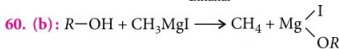
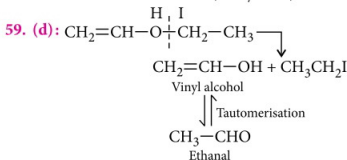
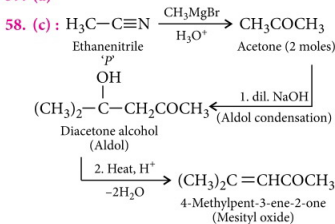
52. (a)



This involves the formation of carbocation as an intermediate.

54. (d) : For an ideal solution; $\Delta H = 0$ and $\Delta V = 0$
From, $\Delta G = \Delta H - T\Delta S$
as $\Delta G = -ve$ hence, $\Delta G < 0$ and $\Delta S > 0$
55. (b) : $\Delta G^\circ = -nFE^\circ$
 $-240000 = -2 \times 96,500 \times E^\circ \Rightarrow E^\circ = 1.24 \text{ V}$
56. (b) : Cupric iodide (CuI_2) is not known and rapidly decomposes to cuprous iodide, Cu_2I_2 and I_2 .

57. (a)



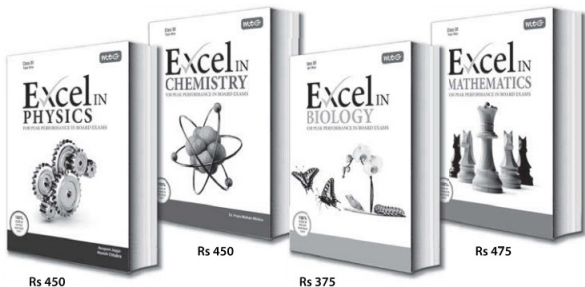
$$1 \text{ mole} = ? \text{ g} \quad 22400 \text{ cm}^3 \text{ at STP}$$

$$0.44 \text{ g} \quad 112 \text{ cm}^3$$

$$\text{Mass of alcohol} = \frac{0.44 \times 22,400}{112} = 88 \text{ g}$$

Alcohol reacts with PCC to give a carbonyl compound which answers silver mirror test. Therefore, alcohol must be primary alcohol which on oxidation with PCC gives aldehyde (carbonyl compound). Therefore, either (b) or (d) is correct. Out of these (b) has the mass 88.

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CHAPTERWISE PRACTICE PAPER

Series-3

Surface Chemistry General Principles & Processes of Isolation of Elements

Time : 3 hrs.

Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
- Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
- Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
- Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
- Use Log Tables, if necessary. Use of calculator is not allowed.

- In chemisorption, why $\frac{x}{m}$ initially increases and then decreases with rise in temperature?
- Give the name of principal ore of copper.
- What is difference between a 'sol' and a 'gel'?
- What is meant by the term pyrometallurgy.
- What is meant by the term 'Peptization'?
- Write the principle of Hydraulic washing.
- Give reason why a finely divided substance is more effective as an adsorbent.
- Why is the froth floatation method selected for the concentration of sulphide ores.
- Giving an example of each, differentiate between multimolecular and macromolecular colloids?
- Describe the role of the following :
 - NaCN in the extraction of silver from a silver ore.
 - Graphite in the electrometallurgy of aluminium from alumina.
- What is adsorption? How does adsorption of a gas on a solid surface vary with pressure? Illustrate with the help of appropriate graph.

- Explain the magnetic separation process.

OR

Explain the froth floatation method.

- Show by a graphical representation, how at a constant pressure a rise in temperature will influence the adsorption of gas on a solid when
 - no compound formation occurs, and
 - chemisorption takes place.
- The values of $\Delta_f G^\circ$ for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1} . Is the reduction of Cr_2O_3 possible with Al?
- Describe and explain, what is observed when
 - a beam of light is passed through a colloidal solution of As_2S_3 .
 - an electric current is passed through a colloidal solution.
- What is electrolytic refining? Give name of a metal that can be refined by this method.
- What is meant by coagulation of a colloidal solution? Name any method by which coagulation of lyophobic sol can be carried out.

18. Out of C and CO, which is a better reducing agent for ZnO?
19. Explain the following observations :
- Lyophilic colloid is more stable than lyophobic colloid.
 - Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
 - Sky appears blue in colour.
20. (i) Name the principal ore of aluminium.
(ii) Describe the leaching of aluminium ore.
21. What are the two classes of emulsions? Give one example of each class. State one activity to test the type of an emulsion.
22. Give reasons for the following :
- Alumina is dissolved in cryolite for electrolysis instead of being electrolysed directly.
 - Carbon and hydrogen are not used as reducing agents at high temperatures.
 - Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction.
23. In coal mines workers are allowed to enter the mines only with mask on their nose.
Now answer the following questions :
- What is the main component of gas mask?
 - Name the process involved in the use of gas mask?
 - What is the value associated with this rule of the coal mines?
24. Describe the role of
- NaCN in the extraction of gold from gold ore.
 - SiO₂ in the extraction of copper from copper matte.
 - Iodine in the refining of titanium.
- Write chemical equations for the reactions involved.
25. What is the effect of size of particles of adsorbent, pressure of gas and prevailing temperature on the extent of adsorption of a gas on a solid?

OR

Explain the terms with suitable examples :

- Alcosol
 - Aerosol
 - Hydrosol.
26. (i) Write the names of two ores of copper.
(ii) Why copper matte is put in silica lined converter?
27. What is the difference between physisorption and chemisorption?
28. (i) Free energies of formation ($\Delta_f G$) of MgO_(s) and CO_(g) at 1273 K and 2273 K are given below :
- $$\Delta_f G(\text{MgO}_{(s)}) = -941 \text{ kJ/mol at } 1273 \text{ K}$$
- $$\Delta_f G(\text{MgO}_{(s)}) = -314 \text{ kJ/mol at } 2273 \text{ K}$$
- $$\Delta_f G(\text{CO}_{(g)}) = -439 \text{ kJ/mol at } 1273 \text{ K}$$
- $$\Delta_f G(\text{CO}_{(g)}) = -628 \text{ kJ/mol at } 2273 \text{ K}$$
- On the basis of the above data, predict the temperature at which carbon can be used as a reducing agent for MgO_(s).
- (ii) Out of C and CO, which is a better reducing agent at 673 K?

OR

- Describe the principle of froth floatation process. What is the role of a stabilizer and depressant? Give one example each.
 - Giving examples, differentiate between roasting and calcination.
29. (i) Derive the mathematical expression or show the relationship between the extent of adsorption of a gas on the surface of a solid (with lower and higher ranges of pressure). Calculate the extent of adsorption at one atmosphere.
- (ii) How does adsorption of a gas on a solid surface vary with (a) temperature and (b) pressure?
Illustrate with the help of appropriate graphs.

OR

- Explain the following terms with a suitable example in each case :
(a) Shape-selective catalysis
(b) Dialysis
- How are the following sols produced :
(a) Sulphur sol (b) Colloidion?

30. Account for the following facts :

- (i) The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.
- (ii) The reduction of Cr_2O_3 with Al is thermodynamically feasible, yet it does not occur at room temperature.
- (iii) Pine oil is used in froth floatation method.

OR

- (i) Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in metallurgy of aluminium. Why?
- (ii) Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.
- (iii) Explain the electrolytic refining for the purification of copper.

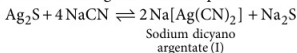
SOLUTIONS

- 1. $\frac{x}{m}$ initially increases because the heat supplied acts as activation energy required in chemisorption and then decreases due to exothermic nature of adsorption equilibrium.
- 2. Principal ore of copper is copper pyrites – CuFeS_2 .
- 3. The colloidal system in which dispersed phase is solid and dispersion medium is liquid is called sol while the colloidal system in which dispersed phase is liquid and dispersion medium is solid is called gel.
- 4. The process of extraction of metal from its ore by heating the metal oxide with a suitable reducing agent is known as pyrometallurgy.
- 5. The process of conversion of freshly prepared precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte is called peptization.
- 6. Hydraulic washing is based on the difference in gravities of the ore and the gangue.
- 7. Surface area of a finely divided substance is larger than when present in the compact form, hence, it is more effective as an adsorbent.

8. Froth floatation method is used for the concentration of sulphide ores because surface of sulphide ore is preferentially wetted by oil while that of gangue is preferentially wetted by water.

9. Multimolecular colloids are formed when several atoms or small molecules of a substance aggregate together to form species having size in the colloidal range (diameter $< 1\text{ nm}$) e.g. gold sol. Macromolecular colloids are formed when macromolecules of colloidal size are dispersed in dispersion medium e.g. protein in water.

10. (i) NaCN combines with argentite ore of silver forming a soluble complex.

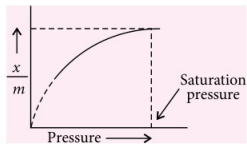


Ag is displaced from this complex when more reactive metal is added to it.

- (ii) The role of graphite in electrometallurgy of Al is to prevent the liberation of O_2 at the anode which may otherwise oxidise some of the liberated Al back to Al_2O_3 .

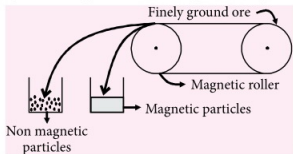
11. Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting in a higher concentration of the molecules on the surface.

Effect of pressure on adsorption of gas : At constant temperature, the adsorption of gas increases with the increase of pressure of the gas. At low pressure, it increases rapidly. At an equilibrium pressure, the extent of adsorption (x/m) reaches its maximum value after which adsorption is independent of pressure.



$$\frac{x}{m} = kP^{\left(\frac{1}{n}\right)}$$

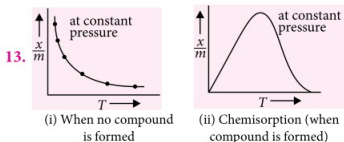
- 12. Magnetic separation process :** This process is based on the difference in magnetic properties of the ore components. If either the ore or the gangue is capable of being attracted by a magnetic field then such separations are carried out (e.g., in case of iron ores). The ground ore is carried on a conveyor belt which passes over a magnetic roller. The magnetic and non-magnetic components form separate heaps.



OR

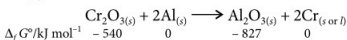
Froth floatation method : The method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non wettability of the mineral particles and froth stabilizers (e.g., cresols, aniline) stabilize the froth.

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and skimmed off.



$\frac{x}{m}$ is extent of adsorption, where 'x' is the mass of adsorbate, 'm' is the mass of adsorbent.

- 14. Reduction of Cr_2O_3 by Al (Thermite process) is**



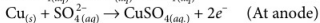
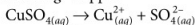
Gibbs energy change for the reduction reaction would be

$$\Delta_r G^\circ = -827 - (-540) = -287 \text{ kJ mol}^{-1}$$

Negative value of $\Delta_r G^\circ$ suggests that the reaction is spontaneous and will occur. However, to initiate the reaction, high temperature is required. Once the reaction starts it goes to completion.

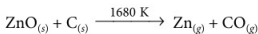
- 15. (i)** The path of light becomes visible due to scattering of light by the colloidal particles. The phenomenon is called Tyndall effect.
(ii) When an electric current is passed through colloidal solution, colloidal particles move towards one of the electrodes depending upon their charge.

- 16. In electrolytic refining, impure metal is made anode and a thin strip of pure metal is made cathode. Solution of salt of same metal is made electrolyte. On passing electricity metal dissolves at anode and is deposited at the cathode. Impurities are left behind as anode mud. e.g. Copper.**



- 17. (i)** The process of settling of colloidal particles into precipitate by aggregating together is called coagulation of colloidal solution.
(ii) Coagulation of a lyophobic sol can be carried out by adding an electrolyte.

- 18. The $\Delta_f G^\circ$ of CO_2 from CO ($\text{CO} \rightarrow \text{CO}_2$) is always higher than that of $\Delta_f G^\circ$ of ZnO . Therefore CO cannot be used for the reduction of ZnO to Zn . Carbon is a better reducing agent giving CO for ZnO at a temperature higher than the temperature where two lines ($\text{C} \rightarrow \text{CO}$ and $\text{Zn} \rightarrow \text{ZnO}$) intersect. Temperature of the order of 1680 K is chosen where zinc vaporises :**



Here, $\Delta_f G^\circ(\text{CO}) < \Delta_f G^\circ(\text{ZnO})$.

- 19. (i)** A lyophilic colloid is stable due to the charge as well as solvation of the sol particles. Such a solution can only be

coagulated by adding an electrolyte and by adding a suitable solvent which can dehydrate the dispersed phase.

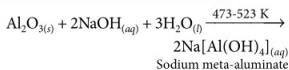
On the other hand, a lyophobic sol is stable due to charge only and hence can be easily coagulated by adding small amount of an electrolyte.

- (ii) Ferric hydroxide solution adsorbs Cl^- ions of NaCl and get neutralised. Thus the colloidal particles get precipitated *i.e.*, ferric hydroxide is precipitated when NaCl solution is added.
- (iii) The atmospheric particles of colloidal range scatter blue component of the white sunlight preferentially. That is why sky appears blue.

20. (i) The principal ore of aluminium is bauxite $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ or $\text{AlO}_x(\text{OH})_{3-2x}$

(ii) Leaching of alumina from bauxite :

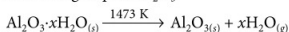
Bauxite usually contains SiO_2 , iron oxide (Fe_2O_3) and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. The Al_2O_3 is leached out as sodium aluminate.



The sodium aluminate is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.



The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give pure Al_2O_3 .



21. The two types of emulsions are :

- (i) **Oil-in-water type** in which small droplets of an oil are dispersed in water.
Example : Milk.
- (ii) **Water-in-oil type** in which water droplets are dispersed in an oil medium.

Example : Butter.

Dye test : Some oil soluble dye is added to the emulsion. If the background becomes coloured and droplets are seen, then the emulsion is water in oil type.

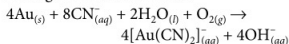
- 22. (i) Alumina is dissolved in cryolite to lower the melting point and improve its electrical conductivity.
- (ii) Carbon and hydrogen react with metals at high temperature forming their carbides and hydrides respectively.
- (iii) In the Ellingham diagram, the (Cu, Cu_2O) curve is almost at the top while (C, CO) and (CO , CO_2) lines lie much below it particularly in the temperature range 500 – 600 K. This means that it is very easy to reduce cuprous oxide to metallic copper by heating with coke rather than heating sulphide ore of copper.

23. (i) The main component of gas mask is activated charcoal.

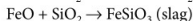
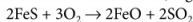
(ii) The process involved in the use of gas mask is adsorption of poisonous gases by activated charcoal.

(iii) Care for human health.

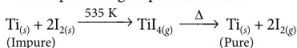
24. (i) NaCN is used for leaching of gold ore in the presence of air to form soluble gold complex from which metal is displaced by adding more reactive metal.



(ii) SiO_2 is added in the extraction of copper from copper matte to remove remaining FeS and FeO as silicate (slag).



(iii) Iodine forms a volatile compound with titanium which on further heating decomposes to give pure titanium.



25. (i) **Effect of size of the particles of adsorbent :** Greater the surface area of the solid available for adsorption per gram of adsorbent,

greater would be its adsorbing power. That is why porous or finely divided forms of adsorbents adsorb more strongly. However, the size of pores should be large enough to allow the diffusion of gas molecules.

- (ii) **Effect of pressure** : A relationship between the amount adsorbed and the equilibrium

pressure is given by $\frac{x}{m} = kP^{\left(\frac{1}{n}\right)}$

Increase in pressure initially increases adsorption which attains equilibrium at high pressure known as saturation pressure.

- (iii) **Effect of temperature** : Adsorption being exothermic decreases with the increase in temperature. This is true for physical adsorption. However, in chemical adsorption the extent of adsorption first increases and then decreases with the increase in temperature.

OR

- (i) Colloidal system having alcohol as the dispersion medium is called *alcosol* e.g. sol of cellulose nitrate in ethyl alcohol.
- (ii) Colloid of a liquid/solid in a gas is called *aerosol* e.g. fog, insecticide sprays, smoke, dust etc.
- (iii) *Hydrosol* is a colloid of solid in water as dispersion medium e.g. starch sol.
26. (i) Main ores of copper are :
(a) Copper pyrites - CuFeS_2
(b) Copper glance - Cu_2S
- (ii) Main components of copper matte are Cu_2S and FeS (obtained from copper pyrites). When a blast of hot air is passed, both are converted into their respective oxides. The converter lined with silica (SiO_2), combines with FeO to form slag thus purifying Cu_2O .
- $$2\text{Cu}_2\text{S}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{Cu}_2\text{O}_{(s)} + 2\text{SO}_{2(g)}$$
- $$2\text{FeS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{FeO}_{(s)} + 2\text{SO}_{2(g)}$$
- $$\text{FeO}_{(s)} + \text{SiO}_{2(s)} \rightarrow \text{FeSiO}_{3(s)}$$
- (Basic) (Acidic) Slag

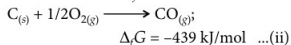
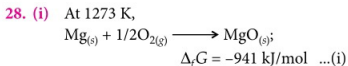
27. Physisorption exists due to weak van der Waals forces while chemisorption takes place due to formation of chemical bonds.

Physisorption is reversible, but chemisorption is irreversible.

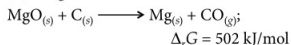
Enthalpy of physisorption is low as compared to chemisorption.

Rate of physisorption decreases with increasing temperature while in case of chemisorption, the rate first increases with increasing temperature and then decreases.

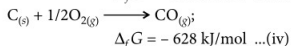
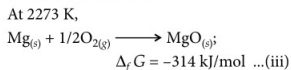
Physisorption is non-specific in nature while, chemisorption is highly specific.



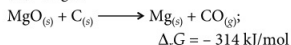
Subtracting equation (i) from equation (ii), we get



As $\Delta_r G$ for the above reduction reaction is positive, therefore, reduction of MgO by C is not feasible at 1273 K.



Subtracting equation (iii) from equation (iv), we get



As $\Delta_r G$ for the above reduction reaction is -ve, therefore, reduction of MgO by carbon at 2273 K is feasible and hence, carbon can be used as a reducing agent.

- (ii) At 673 K (low temperature), the $\Delta G^\circ(\text{CO}, \text{CO}_2)$ line lies below $\Delta G^\circ(\text{C}, \text{CO}_2)$ line in the Ellingham diagram. Therefore, at 673 K, CO is a better reducing agent. On the other hand, at higher temperature, $\Delta G^\circ(\text{C}, \text{CO}_2)$ line lies below $\Delta G^\circ(\text{CO}, \text{CO}_2)$ line and hence at a higher temperature carbon is better reducing agent than CO .

OR

- (i) **Froth floatation method** : This is used for the dressing of lighter ores (mainly sulphide ores).

The process is based on the different wetting properties of ore and gangue particles.

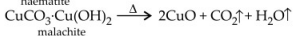
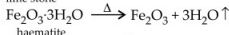
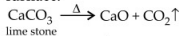
Finely powdered ore is mixed with water and to it collectors and froth stabilisers are added. The mixture is finely agitated by passing compressed air through it. The oil reduces the surface tension and the sulphide ore which is preferentially wetted by oil comes in froth leaving behind heavy matter of gangue wetted by water. The froth being lighter rises to the surface and is skimmed off.

Collectors (e.g. pine oil, fatty acids) enhance the non-wettability of the mineral particles.

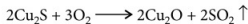
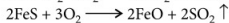
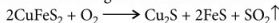
Stabilizers (e.g. cresols and aniline) stabilize the froth.

Depressants are used to prevent one type of sulphide ore particles from forming the froth if ore contains sulphides of two metals.

- (ii) **Calcination** involves simple decomposition of ore on heating below its melting point usually in absence of air to produce new compounds having higher percentage of metal as well as to remove the moisture, organic matter and volatile impurities, e.g., CO_2 . Calcination makes the ore porous and is carried out in reverberatory furnace.



Roasting involves action of heat in limited supply of air below its melting point to produce other chemical changes along with decomposition. The ore lose sulphur as oxide leaving behind oxide of metal.



Roasting is usually done in reverberatory furnace with vents kept open.

29. (i) $\frac{x}{m} \propto p^1$ at low pressure where 'x' is mass of adsorbate and 'm' is mass of adsorbent.

$$\frac{x}{m} \propto p^0 \text{ at high pressure}$$

$$\frac{x}{m} \propto p^{1/n} \text{ at moderate}$$

pressure where $\frac{1}{n}$ lies between 0 and 1.

$$\frac{x}{m} = kp^{1/n}$$

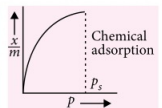
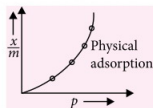
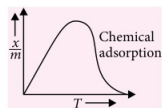
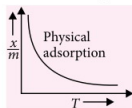
$$\text{At 1 atm, } \frac{x}{m} = k(1)^{1/n} \Rightarrow \frac{x}{m} = k$$

At 1 atm, extent of adsorption is equal to 'k' (constant).

- (ii) Physical adsorption of a gas on solid decreases with increase in temperature and increases with increase in pressure.

Chemical adsorption first increases and then decreases with increase in temperature.

Chemical adsorption first increases and then becomes independent of pressure with increase in pressure. $\frac{x}{m}$ represents extent of adsorption where x is mass of adsorbate, m is mass of adsorbent.



OR

- (i) (a) **Shape-selective catalysis** : It depends on the pore structure. Zeolites are generally used as catalysts. Depending

on the size of the reactant and product molecules compared to the size of the pores of the zeolites, reaction proceeds in a particular manner.

(b) **Dialysis** : It is a process to separate a crystalloid from a colloid by diffusion through a semipermeable membrane.

(ii) (a) Sulphur sol is obtained by bubbling H_2S gas through an oxidising agent like bromine water.



(b) Cellulose nitrate colloid can be prepared by dispersing it in a mixture of ethyl alcohol and ether. The 4% solution of it is known as collodion.

30. (i) For the reduction process the value of entropy change (ΔS) is more positive when the metal formed is in liquid state and metal oxide being reduced is in solid state. Thus, the value of free energy change (ΔG°) becomes more negative and the reduction becomes easier.

(ii) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
 ΔG° is -ve for this reaction
 $\Delta G^\circ = -RT \ln K$ i.e., the interpretation of ΔG° is based upon K (equilibrium constant). Since in the above redox reaction, all the reactants and products are solid at room temperature, therefore it does not take place at room temperature. However at high temperature, when chromium melts, the reaction proceeds rapidly as the value of $T\Delta S$ increases and $\Delta_r G^\circ$ becomes more negative.

(iii) Pine oil acts as collector which enhances the non-wettability of the ore particles.

OR

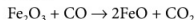
(i) Below the temperature 1623 K corresponding to the point of intersection of Al_2O_3 and MgO curves in Ellingham diagram magnesium can reduce alumina but magnesium is a very expensive metal than aluminium and the process will be quite uneconomical.

(ii) (a) **Combustion zone** : In the lowest part of the furnace temperature is about $1500-1600^\circ\text{C}$. In this zone carbon burns in presence of hot air.



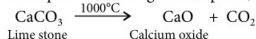
Carbon dioxide rises upward and reduced to carbon monoxide with red hot coke.

(b) **Reduction zone** : In this zone in the uppermost part of the furnace temperature is about $250-700^\circ\text{C}$. In this zone metal oxide is reduced to metal.

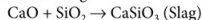


Iron formed is called spongy iron.

(c) **Slag formation zone** : In the central zone temperature is $800-1000^\circ\text{C}$. Lime stone present in charge decomposes,

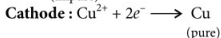
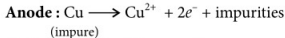


Calcium oxide acts as a flux and combines with silica (gangue) present to form slag.



(d) **Melting zone** : Just above the combustion zone temperature is nearly $1200-1500^\circ\text{C}$. The spongy iron melts at 1300°C and collects at bottom of the hearth. The slag being lighter floats over the molten iron. The slag and molten ore are removed from their respective holes.

(iii) Impure copper can be purified by electrolytic refining. The anode is made of impure copper while cathode is made up of pure copper. Electrolyte is the solution of metal salt. On passing electricity, the metal from the anode goes into the solution as Cu^{2+} ions while pure metal gets deposited at the cathode. The impurities settle down below anode as anode mud. The reactions involved are





EXAMINER'S MIND NCERT^{CLASS} XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

SURFACE CHEMISTRY | THE *p*-BLOCK ELEMENTS (Group 15 to 18) | THE *d*- AND *f*-BLOCK ELEMENTS

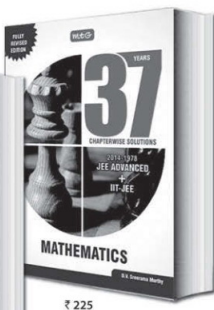
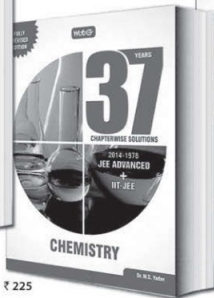
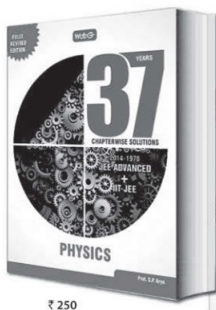
SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- 0.2 g of fine animal charcoal is mixed with half litre of acetic acid (1 M) solution and shaken for 30 minutes.
(a) Concentration of the solution remains same.
(b) Concentration of the solution increases.
(c) Concentration of the solution decreases.
(d) None of these.
- On heating ammonium dichromate and barium azide separately we get
(a) N_2 in both cases
(b) N_2 with ammonium dichromate and NO with barium azide
(c) N_2O with ammonium dichromate and N_2 with barium azide
(d) N_2O with ammonium dichromate and NO_2 with barium azide.
- Aqueous solutions of hydrogen sulphide and sulphur dioxide when mixed together, yield
(a) sulphur trioxide and water
(b) hydrogen and sulphurous acid
(c) sulphur and water
(d) hydrogen peroxide and sulphur.
- Which of the following orders is not in accordance with the property stated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power
(c) $HI > HBr > HCl > HF$: Acidic property in water
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity
- First compound of Xe synthesized was
(a) $[XeF]^+[XePtF_5]^-$ (b) $[XeO_2]$
(c) $Xe[PtF_6]$ (d) $O_2[XeF_6]$
- Which one of the following does not occur as sulphide ore?
(a) Zn (b) Cr
(c) Ag (d) Fe
- Which one of the following ionic species will impart colour to an aqueous solution?
(a) Zn^{2+} (b) Cu^+
(c) Ti^{4+} (d) Cr^{3+}
- For the adsorption of a gas on a solid, the plot of $\log x/m$ versus $\log P$ is linear with slope equal to
(a) k (b) $\log k$
(c) n (d) $1/n$
- P_2O_5 is an anhydride of
(a) H_3PO_4 (b) $H_2P_2O_7$
(c) H_3PO_3 (d) HPO_3
- When SO_2 is passed through acidified $K_2Cr_2O_7$ solution
(a) the solution turns blue
(b) the solution is decolourised
(c) SO_2 is reduced
(d) green $Cr_2(SO_4)_3$ is formed
- Which of the following is the strongest Brønsted base?

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- (a) ClO^- (b) ClO_4^-
(c) ClO_3^- (d) ClO_2^-
12. Sea-diver goes deep in the sea with a mixture of which of the following gases ?
(a) O_2 and CO_2 (b) O_2 and He
(c) CO_2 and Ar (d) O_2 and Ar
13. Identify the statement which is not correct regarding copper sulphate.
(a) It reacts with NaOH and glucose to give Cu_2O .
(b) It gives CuO on strong heating in air.
(c) It reacts with KCl to give Cu_2Cl_2 .
(d) It reacts with KI to give iodine.
14. Which of the following lanthanide ions is paramagnetic ?
(a) Ce^{4+} (b) Yb^{2+}
(c) Lu^{3+} (d) Eu^{2+}
15. Bredig's arc method cannot be used to prepare colloidal solution of which of the following metals ?
(a) Pt (b) Fe
(c) Ag (d) Au
16. The decreasing order of boiling points of the following hydrides is
(a) $\text{H}_2\text{O} > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
(b) $\text{H}_2\text{O} > \text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
(c) $\text{H}_2\text{O} > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
(d) $\text{H}_2\text{O} > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{NH}_3$
17. Which of the following statements is correct ?
(a) SF_6 does not react with water.
(b) OF_6 is d^2sp^3 -hybridized.
(c) $\text{S}_2\text{O}_3^{2-}$ is a linear ion.
(d) There is no π -bonding in SO_4^{2-} .
18. Which of the following increasing orders is not correct as mentioned in the property with it ?
(a) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
(Thermal stability)
(b) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
(Oxidising power)
(c) $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
(Reducing nature)
(d) $\text{HIO}_4 < \text{ICl} < \text{I}_2 < \text{HI}$
(Oxidation number of iodine)

19. Which of the following noble gases is most soluble in water ?
(a) He (b) Ar
(c) Ne (d) Xe
20. Although zirconium belongs to $4d$ -transition series and hafnium belongs to $5d$ -transition series even then they show similar physical and chemical properties because
(a) both belong to d -block
(b) both have same number of electrons
(c) both have similar atomic radius
(d) both belong to the same group of the periodic table.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. The size of the colloid particles is
(a) $>$ suspension particles
(b) $<$ suspension particles
(c) $>$ true solution particles
(d) $<$ true solution particles.
22. Catalyst(s) used in Contact process of manufacture of sulphuric acid is/are
(a) $\text{NO}_{(g)}$ (b) V_2O_5
(c) Mo (d) platinised asbestos.
23. Which among the following statements is/are correct?
(a) XeF_4 and SbF_5 combine to form a salt.
(b) He and Ne do not form clathrates.
(c) He has lowest boiling point in its group.
(d) He is used as a filler in electric transformers.
24. In which of the following S - S link is present ?
(a) Caro's acid (b) Dithionic acid
(c) Thiosulphuric acid (d) Marshall's acid
25. Which of the following alloys contain(s) Cu and Zn?
(a) Bronze (b) Brass
(c) Gun metal (d) Type metal

SECTION - III

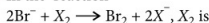
Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX' , XX'_3 , XX'_5 and XX'_7 where X is a larger size halogen and X' is smaller size halogen.

26. In the reaction



- (a) Cl_2 (b) Br_2
(c) I_2 (d) N_2

27. Which bond is most polar ?

- (a) $Cl-F$ (b) $Br-F$
(c) $I-F$ (d) $F-F$

28. When I_2 is passed through KCl , KF and KBr solutions

- (a) Cl_2 and Br_2 are evolved
(b) Cl_2 is evolved
(c) Cl_2 , Br_2 and F_2 are evolved
(d) None of these.

Paragraph for Questions 29 to 31

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii is not quite regular as it is regular in M^{3+} ions.

29. The correct order of ionic radii of Ce, La, Pm and Yb in +3 oxidation state is

- (a) $La^{3+} < Pm^{3+} < Ce^{3+} < Yb^{3+}$
(b) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(c) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(d) $Yb^{3+} < Ce^{3+} < Pm^{3+} < La^{3+}$

30. Lanthanoid contraction is due to increase in

- (a) atomic number
(b) effective nuclear charge
(c) atomic radius
(d) valence electrons.

31. The lanthanide contraction is responsible for the fact that

- (a) Zr and Y have about the same radius
(b) Zr and Hf have about the same radius
(c) Zr and Nb have similar oxidation state
(d) None of these.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists :

List I (Property)	List II (Reason)
P. Brownian movement	1. Due to the scattering of light
Q. Tyndall effect	2. Due to the presence of charge
R. Electrophoresis	3. Due to the neutralisation of charge
S. Coagulation	4. Due to unequal bombardment by solvent molecules

P	Q	R	S
(a) 4	3	2	1
(b) 1	2	3	4
(c) 3	1	4	2
(d) 4	1	2	3

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. An element which can show +8 oxidation state	1. Ce
Q. An element with +7 as the most stable oxidation state in its oxides	2. Pm
R. Radioactive lanthanoid	3. Os
S. Lanthanoid which shows +4 oxidation state	4. Mn

	P	Q	R	S
(a)	1	2	3	4
(b)	2	3	4	1
(c)	4	1	2	3
(d)	3	4	2	1

34. Match the List I with List II and select the correct answer using the code given below the lists :

	List I (Property)	List II (Metal)
P.	Element with highest second ionisation enthalpy	1. Cr
Q.	Element with highest third ionisation enthalpy	2. Cu
R.	M in $M(\text{CO})_6$ is	3. Zn
S.	Element with highest enthalpy of atomisation	4. V

	P	Q	R	S
(a)	2	3	1	4
(b)	4	3	1	2
(c)	3	1	2	4
(d)	1	2	3	4

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.

35. **Assertion** : Lyophilic sols are reversible sols.

Reason : Lyophilic sols can be reconstituted by simply remixing the dispersed phase and dispersion medium.

36. **Assertion** : In transition elements ns orbital is filled up first and $(n-1)d$ afterwards, during ionisation ns electrons are lost prior to $(n-1)d$ electrons.

Reason : The effective nuclear charge felt by $(n-1)d$ electrons is higher as compared to that by ns electrons.

37. **Assertion** : All F—S—F bond angles in SF_4 are greater than 90° but less than 180° .

Reason : The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion.

38. **Assertion** : F atom has less negative electron gain enthalpy than Cl atom.

Reason : Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F atom.

39. **Assertion** : Although PF_5 , PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.

Reason : Phosphorus has lower electronegativity than nitrogen.

40. **Assertion** : Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason : Actinoids can utilise their $5f$ orbitals along with $6d$ orbitals in bonding but lanthanoids do not use their $4f$ orbital for bonding.

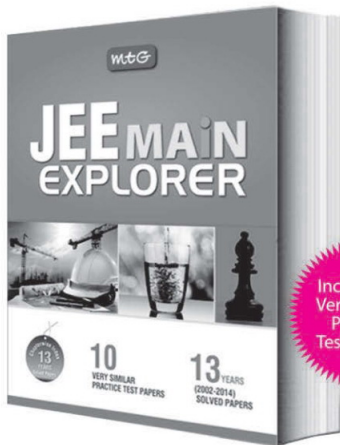
SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

- Graph between $\log(x/m)$ and $\log(P)$ is a straight line at an angle of 45° with an intercept on y -axis 0.3010. The amount of the gas adsorbed per gram of the adsorbent is $x \times 10^2$ mg when pressure is 0.2 atm. The value of x is
- The total number of P—O—P and P—O—H bonds present in pyrophosphoric acid is
- When SO_2 is passed in an acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, the oxidation state of sulphur is changed to
- Number of S—O—S bonds in S_3O_9 is
- Number of lone pair of electrons in XeF_4 is
- The difference between number of σ and π bonds in peroxodisulphuric acid is

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47. In a given sample of bleaching powder, the percentage of available chlorine is 49. The volume of chlorine obtained if 10 g of the sample is treated with HCl at N.T.P. is $x/2$. The value of x is
48. Desorption activation energy of a solid surface is 150 kJ mol^{-1} , if a hydrogen atom remains on the surface of a solid for $x \times 10^5$ years at 298 K, the value of x is [Assume that $\tau_0 = 10^{-13} \text{ s}$.]
49. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is
50. The number of moles of KMnO_4 reduced by one mole of KI in alkaline medium is

SOLUTIONS

1. (c) : Concentration of the solution decreases on adding fine animal charcoal to acetic acid solution because acetic acid gets adsorbed on charcoal.
2. (a) : $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 $\text{Ba}(\text{N}_3)_2 \xrightarrow{\Delta} \text{Ba} + 3\text{N}_2$
3. (c) : SO_2 oxidises moist hydrogen sulphide to sulphur.
 $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$
4. (a) : The bond dissociation energy order is incorrect, the correct order is $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$. The lower value of bond dissociation energy of fluorine is due to the high inter-electronic repulsions between non-bonding electrons in the $2p$ -orbitals of fluorine. As a result, $\text{F}-\text{F}$ bond is weaker in comparison to $\text{Cl}-\text{Cl}$ and $\text{Br}-\text{Br}$ bonds.
5. (c) : $\text{Xe}[\text{PtF}_6]$ was first real compound of any of the noble gases.
6. (b) : Zinc exists as zinc blende, ZnS . Silver exists as silver glance, Ag_2S . Iron exists as iron pyrites, FeS_2 . Chromium does not exist as sulphide ore but it is in the form of chromite ore i.e., $\text{FeO.Cr}_2\text{O}_3$.
7. (d) : Electronic configuration of $\text{Cr}^{3+}(24)$ is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$

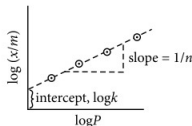
As Cr^{3+} ion has three unpaired electrons in its valence shell, so it imparts green colour to an aqueous solution.

8. (d) : Apply, $\frac{x}{m} = kP^{1/n} \dots (i)$

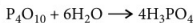
Take log on both sides of equation (i)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

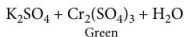
Thus, a graph between $\log(x/m)$ and $\log P$, will give a straight line of slope $1/n$ and intercept $\log k$ as shown.



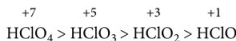
9. (a) : P_2O_5 is an anhydride of phosphoric acid (H_3PO_4).



10. (d) : $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \rightarrow$
 Orange



11. (a) : Acidic strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen,

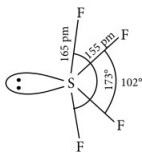


Since HClO_4 is the strongest acid, its conjugate base is the weakest base and HClO is the weakest acid, its conjugate base is the strongest base.

12. (b) : Helium is not soluble in blood even under high pressure, a mixture of 80% helium and 20% oxygen is used instead of ordinary air, by sea-divers for respiration.

13. (c)

14. (d) : $\text{Ce} \rightarrow [\text{Xe}] 4f^1 5d^1 6s^2$; $\text{Ce}^{4+} \rightarrow [\text{Xe}]$
 $\text{Yb} \rightarrow [\text{Xe}] 4f^{14} 6s^2$; $\text{Yb}^{2+} \rightarrow [\text{Xe}] 4f^{14}$
 $\text{Lu} \rightarrow [\text{Xe}] 4f^{14} 5d^1 6s^2$; $\text{Lu}^{3+} \rightarrow [\text{Xe}] 4f^{14}$
 $\text{Eu} \rightarrow [\text{Xe}] 4f^7 6s^2$; $\text{Eu}^{2+} \rightarrow [\text{Xe}] 4f^7$



Trigonal bipyramidal structure of SF_4 .

38. (c) : Due to the small size of fluorine atom, electron density is high which hinders the addition of an extra electron.

39. (b) : Nitrogen can show a maximum covalency of 4 because of absence of d -orbital in valence shell.

40. (c)

41. (4) : $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$

$$\frac{1}{n} = \tan 45^\circ = 1$$

$$\log k = 0.3010$$

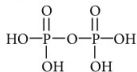
$$\text{So, } n = 1 \text{ and } k = 2$$

$$\frac{x}{m} = k P^{1/n} = 2(0.2)^1 = 0.4 \text{ g}$$

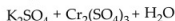
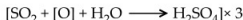
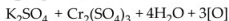
$$= 4 \times 10^2 \text{ mg}$$

$$\text{So } x = 4$$

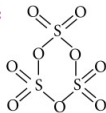
42. (5) : $1 + 4 = 5$



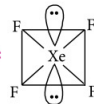
43. (6) : $\text{K}_2\text{Cr}_2\text{O}_7$ acts as a strong oxidising agent. It oxidises other compounds and itself gets reduced. In SO_2 , S is in +4 state so it gets oxidised to +6 state which is its maximum oxidation state.



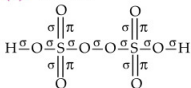
44. (3) :



45. (2) :



46. (7) : $11 - 4 = 7$



47. (3) : 10 g bleaching powder will produce 4.9 g Cl_2

$$\frac{4.9 \times 22.4}{71} \text{ litre of } \text{Cl}_2 \text{ at NTP} = 1.5 \text{ litre}$$

$$\text{i.e., } \frac{x}{2} = 1.5 \Rightarrow x = 3$$

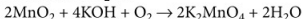
48. (6) : $\tau = \tau_0 e^{E_a / RT}$

$$E_a = 150 \text{ kJ/mol, } \tau_0 = 10^{-13} \text{ s}$$

$$\tau = 10^{-13} \exp \left(\frac{150 \times 10^3}{8.314 \times 298} \right) = 10^{-13} (e^{60.5})$$

$$= 1.9 \times 10^{13} \text{ s} = 6 \times 10^5 \text{ years} \Rightarrow x = 6$$

49. (6) : The chemical reaction of alkaline oxidative fusion of MnO_2 is :

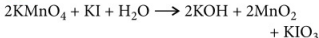


The oxidation state of Mn in product, K_2MnO_4 is :

Let oxidation state of Mn be x .

$$\therefore x + 4(-2) = -2 \Rightarrow x = +6$$

50. (2) : In alkaline medium :



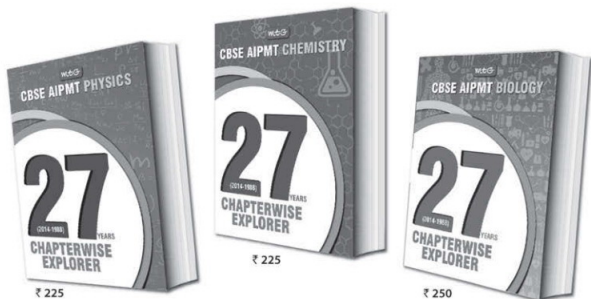
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Q1. Why Hg exists as Hg_2^{2+} ?

— Biswajit Mandal

Ans. Mercury (chemical symbol, Hg) is a heavy metal occurring in several forms :

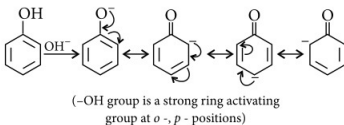
- Hg^0 : (Oxidation state '0'); Exists as vapour or as liquid metal.
- Hg_2^{2+} (Mercurous) : (Oxidation state +1); Exists as inorganic salts.
- Hg^{2+} (Mercuric) : (Oxidation state +2); Exists either inorganic salts or organo-mercury compounds.

The reason for the existence of Hg_2^{2+} ion is as, Hg_2^{2+} which is two Hg^+ ions bonded together like, $\text{Hg}^+ - \text{Hg}^+$. However, Hg^+ by itself does not exist. Therefore, mercury (I) ion exists as Hg_2^{2+} .

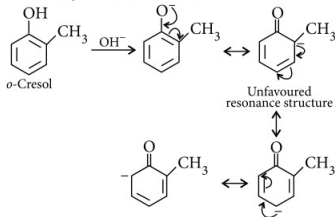
Q2. Why *m*-cresol exists? When -OH group is a ring activating group and hence, should be *o*-, *p*-directing.

— Navdeep Kumar, Amritsar

Ans. In phenol, the -OH group (electron withdrawing) is directly attached to the benzene ring. This allows resonance stabilization of the anion formed by loss of the hydroxyl proton.

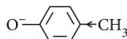


Whereas, $-\text{CH}_3$ group (electron donating group) has +I as well as hyperconjugation effects, both of which increase the electron density in the O-H bond.



($-\text{CH}_3$ is a weak ring activating group at *o*-, *p*-positions as compared to -OH)

But, hyperconjugation can operate only at *o*- and *p*-positions while +I effect operates at all the three positions.



Charge on oxygen intensified
(less stable than phenoxide)

Hence, $-\text{CH}_3$ exist at *m*-position (due to +I effect) in phenol and forms *m*-cresol (3-methylbenzenol)



Q3. Does ice melt faster in water (soft drink) or air?

— Poonam Jaiswal, Alwar

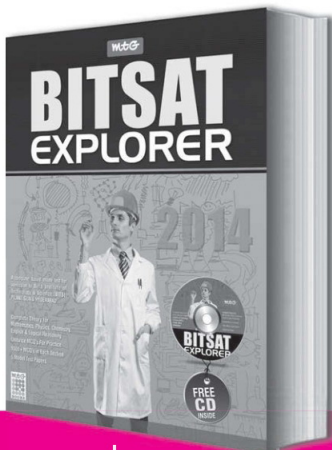
Ans. Ice is a solid form of water. The two chemical processes are involved in melting of ice : one is transfer of heat energy and another is breakdown of bonds between H_2O molecules (*i.e.* in solid and liquid). When ice cubes are exposed to the water, lot of heat energy transferred from the surroundings than in air (low heat capacity). This heat transfer causes the breakdown of H-bonds between H_2O molecules, until all of the solid (ice) has turned into liquid (water). Hence, the ice melts faster in water than in air.



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CHEMISTRY Musing

SOLUTION SET 12

1. (c): Empirical formula of A

Element	C	H	N	O
% age	49.32	9.59	19.18	21.91
Relative no.	49.32/12	9.59/1	19.18/14	21.19/16
of moles	= 4.11	= 9.59	= 1.37	= 1.32
Simplest molar ratio	4.11/1.32 = 3	9.59/1.32 = 7	1.37/1.32 = 1	1.32/1.32 = 1

∴ Empirical formula of A = C₃H₇NO

Empirical formula weight

$$= 3 \times 12 + 7 \times 1 + 1 \times 14 + 1 \times 16 \\ = 36 + 7 + 14 + 16 = 73$$

Molecular weight of B

meq. of Ag = meq. of Ag salt

$$\text{or } \frac{\text{Weight of Ag}}{\text{Eq. wt. of Ag}} = \frac{\text{Weight of salt}}{\text{Eq. wt. of salt}}$$

$$\text{or } \frac{59.67}{108} = \frac{100}{\text{Eq. wt. of salt}}$$

$$\text{or } \text{Eq. wt. of salt} = \frac{100 \times 108}{59.67} = 181$$

Eq. wt. of salt = Eq. wt. of Ag + Eq. wt. of anion

$$\text{or } \text{Eq. wt. of anion} = \text{Eq. wt. of salt} - \text{Eq. wt. of Ag} \\ = 181 - 108 = 73$$

For monobasic acid:

Molecular weight of acid = 73 + 1 = 74

B being monobasic can be represented as

C_nH_{2n+1}COOH.

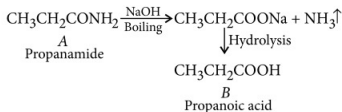
$$74 = n \times 12 + (2n + 1) \times 1 + 1 \times 12 + 2 \times 16 + 1 \times 1 \\ = 12n + 2n + 1 + 12 + 32 + 1 = 14n + 46$$

$$\text{or } 14n = 74 - 46 \text{ or } n = 28/14 = 2$$

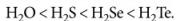
∴ B is C₂H₅COOH.

Structure of A

Since B is obtained by action of A with NaOH followed by hydrolysis so A is an amide.

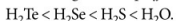


2. (d): Increasing order of acidity is



$$\text{As } pK_a \propto \frac{1}{\text{acidity}}$$

Thus, increasing order of pK_a values is



3. (a): HCOOH → HCOO⁻ + H⁺

$$0.2(1 - \alpha) \quad 0.2\alpha \quad 0.2\alpha$$

$$\therefore [\text{H}^+] = 0.2\alpha$$

$$\text{or } \alpha = \frac{[\text{H}^+]}{0.2} = \frac{6.4 \times 10^{-3}}{0.2} \text{ or } 3.2 \times 10^{-2}$$

So we find that α (degree of dissociation) of HCOOH is very low, on addition of sodium formate the dissociation of HCOOH (weak electrolyte) will be suppressed due to common ion effect.

Since degree of dissociation is very low which has been further suppressed and so we can now neglect it and can take the [HCOOH] as 0.2 M.



Initial	1	0	0
Equi.	0.25	0.75	0.75

$$\therefore [\text{HCOO}^-] = 0.75$$

It is an acidic buffer containing formic acid (HCOOH) and its salt (HCOONa) so its pH is given by

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= -\log(2.4 \times 10^{-4}) + \log \frac{0.75}{0.20} = 4.19 \end{aligned}$$

4. (b): Let velocity (v) = x

Then de Broglie wavelength (λ) = 100 x

$$\text{Now, } \lambda = \frac{h}{mv} \quad \therefore 100x = \frac{h}{mx}$$

$$\text{or } x^2 = \frac{1}{100m} \quad \text{or } x = \frac{1}{10} \sqrt{\frac{h}{m}}$$

$$\text{Hence, } \lambda = 100x = 10 \sqrt{\frac{h}{m}}$$

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